ABSTRACT

Title: BALTIMORE SUPERSITE: HIGHLY TIME AND SIZE RESOLVED CONCENTRATIONS OF URBAN PM2.5 AND ITS CONSTITUENTS FOR RESOLUTION OF SOURCES AND IMMUNE RESPONSES

REVISION 1, December 15, 1999

Investigators:

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Project Period: January 1, 2000 to December 31, 2003

Project Cost: \$3,400,000

PROJECT SUMMARY

We propose to conduct a Supersite project in Baltimore to provide an extended, highly time, size, and compositionally resolved data set, including an indicator of cardiopulmonary response in support of testing hypotheses relating to source attribution and health effects of PM. Such information is needed to support development of State Implementation Plans and the setting of National Ambient Air Quality Standards. Specific hypotheses involve investigations of the toxicity of aerosol components as affected by age, industrial vs urban character, and seasonal differences in source terms and atmospheric chemistry. The toxicological metrics chosen, i.e., cytokine and reactive oxygen species (ROS) assays, will be used in correlations with PM metrics, in much the same manner as EPA's Integrated Air Cancer Program used mutagenicity assays to apportion ambient PM mutagenicity among air pollution sources. The project will encompass hourly resolved cytokine/ROS assays of PM2.5 as a metric of toxic response; along with similarly time-resolved measurements of PM mass, number vs size distribution, light-scattering coefficient; PM sulfate, nitrate, organic carbon, and elemental carbon using commercial continuous and semicontinuous monitors. In addition, three important new instruments will be fielded: UMCP's semicontinuous monitor for quantitatively determining aerosol metals and trace elements; UDE's third generation single particle mass-spectrometric analysis system (RSMS III) for continuous size and semiquantitative determination of individual aerosol particle constituents, from 10 nm to 2.5 µm; and JHU's advanced 3 wavelength LIDAR for three dimensional mapping of Baltimore's wind fields and aerosol concentrations, including plumes from discrete sources. Traditional 24-hr collections for FRM mass and

selected aerosol constituents will provide the link with PM network data. Extensive exploratory organic compound analyses will be performed to reveal the presence of potentially useful tracer species for receptor modeling, and identities and concentrations of potentially toxic PM organic constituents, especially, water soluble polar organic compounds which might contribute to cardiopulmonary-related responses. Gram quantities of PM2.5 will be collected weekly and archived for subsequent use by the research community

The Highly-time (hourly and subhourly) size, and species resolved composition metrics will permit resolution of their contributions by sources, thus, providing the link between the health effects metric and sources. Source allocations will be reinforced by inclusion of the standard meteorological data in the multivariate analyses and 3-dimensional wind field and particle concentration maps. Plume width and, thus, time of influence on a fixed site increases with increasing distance from the source. Thus, with highly time-resolved pollutant metrics local (even individual), more distant, and regional source contributions will likely be readily resolved into different factors by multilinear regression and advanced factor analysis techniques. The 3-D maps will powerfully and visually document the movement of particles from the sources to the receptor, and ultimately improve our understanding of atmospheric stability and seasonal-mesoscale flow patterns in driving aerosol fields over Baltimore city. Note that Baltimore, like most of the large northeastern deepwater port cities, experiences highly complicated local flow patterns which make source-based modeling extremely difficult.

Time-resolved rotating drum impactors (RDI) will be used to separate fresh accumulation aerosol from nearby sources from aged and cloud processed aerosol, and from tailing coarse particle fractions. The spectra determined from RDI measurements will be used to confirm plume "hits" and as a calibration reference for single particle measurements. Cytokine and ROS assays on selected RDI samples will be performed to investigate differences in aerosol age. Mulitvariate calibration models will be used to statistically interpret and interrelate data developed by the variety of new and established techniques. Professor Hopke will utilize his considerable experience in both aerosol measurements and advanced data analysis methods (MLR, PLS, and back propagation neural networks), to provide these critical data analyses.

The equipment will be installed in trailers and deployed to a primary urban site, an industrially influenced urban residential site, and community sites, in support of hypotheses suggested above. Measurements will be made continuously over a 12 month period and will encompass 45-day intensive campaigns to be conducted in summer and winter in South Baltimore to test hypotheses regarding effects of industrial influence and source resolving power of our measurement strategy.

The influence of emissions from source regions at various distances, the variety and severity of local sources, the rich regional and interpretive contexts provided by the IMPROVE site at the Shenandoah National Park, the NARSTO upper air station at Ft. Meade, and abundance of prior regional source attribution studies make Baltimore an excellent location for the proposed measurements and hypothesis testing. Given the severity of diverse sources in close proximity to densely populated areas combined with the complex wind fields, the Baltimore community of scientists and regulators desperately needs the extensive, array of high-quality data which we propose to develop.

Supplemental Keywords: Receptor modeling, aerosol particles, trace elements

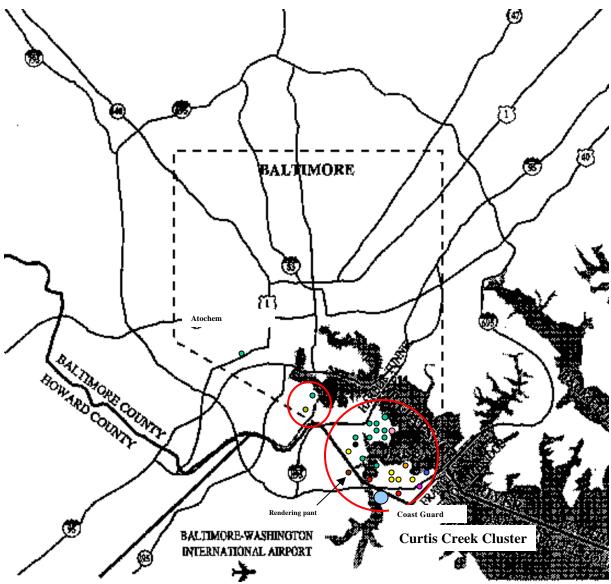
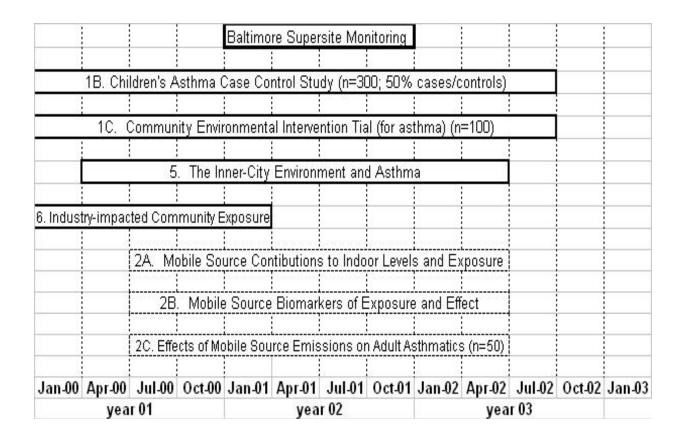
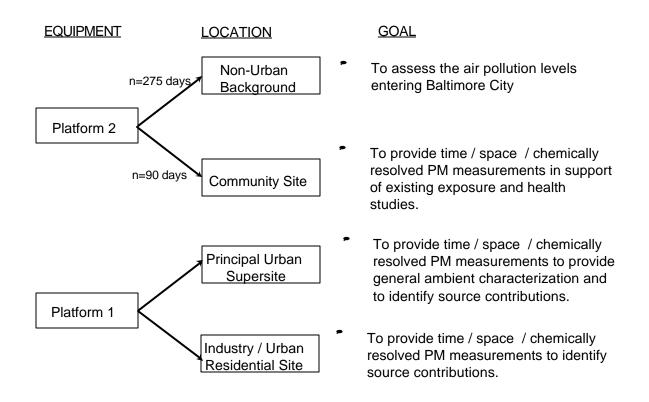


Figure 1. Map of Baltimore showing many of the sources clustered around Curtis Creek and west of the Middle River. Green dots are chemical plants; red, medical waste or sludge incinerators; yellow are land fills; and brown, a rendering plant.





Summary of Proposed Measurements

Instrument/Sampler		Instrument	Sites	Frequency	Duration
Commercial Continuous/Semicontinuous Monitors					
Ultrafine/near accumulation aerosol	0.02 to 0.5 µm	Scanning Mobility Particle Spectrometer, Forward Scanning Laser Spectrometer	1,2	5 min	12 months
Far accumulation aerosol/coarse size spectrum	$0.5 \text{ to} > 10 \mu \text{m}$	Optical Particle Counter	1,2	5 min	12 months
Accumulation aerosol vs. aerodynamic size spectra	$0.5 \text{ to} > 10 \mu\text{m}$	Aerodynamic Particle Spectrometer	2	5 min	Intensives
Light Scattering	entire range	Integrated Nephalometer, Radiance Res.	1,2	2 sec	12 months
Mass concentration	PM2.5	TEOM, 1400A	1,2	5 min	12 months
Sulfate concentration	PM2.5	To be determined (e.g. R&P, HSPH)	1,2	10 min	12 months
Nitrate concentration	PM2.5	To be determined (e.g. R&P, HSPH)	1,2	10 min	12 months
EC/OC	PM2.5	R&P Series 5400-99-004-743-0025	1,2	30 to 60 min	12 months
Temp (2 heights), RH, Wind speed and direction, barometric pressure, solar insulation		RM Young/Campbell Sci. met station	1,2		12 months
Sensible latent heat and momentum fluxes		3-D Sonic Annemometer & Krypton hygrometer	1		12 months
Ozone		TECO	1		12 months
NOx, NO ₂ , NO		TECO	1		12 months
SO_2		TECO	1		12 months
VOC		Hewlet Packard GC	1		12 months
Special Measurements			1	1 hr	12 months
As, Cu, Mn, Ni, Cr	PM2.5	UMCP SEAS	1	1 hr	12 months
Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, V, Ti, Be, Ba Single particle classification by composition and size (PM2.5	UMCP SEAS, retrospective analysis	1	1 hr	Intensives
metals,e.g., Na, Mg, K, Cr, Cu, Zn, Cd, Cs, La, Pb, som valence information, NH ₄ SO ₄ , sulfites, hydroxymethal sulfonic acid, methane sulfonic acid, EC/OC, polynucles aromatic hydrocarbons) 2.5 μm	ne	UDE RSMS III	1	approx 1 min every 10 min	12 months
3-D PM/wind fields, and mixing height		JHU 3-wavelength Lidar	area	1 scan every 6	12 months
				hrs	
210° scan at 5° intervals horizontal by 75° vertical, 8 km		JHU Eye-Safe Lidar	area	1 scan every hour	Intensives
210° scan at 1/2° intervals horizontal by 75° vertical, 8	km range	JHU Eye-Safe Lidar	area	1 scan every hour	Intensives
Selective plume mapping and time series scans		JHU Eye-Safe Lidar	area	1 scan every hour	Intensives
Collections for Off-Line Analyses					
FRM Mass Conc.	<2.5 μm	RAAS 2.5 - 100	1,2	24 hr	12 months
Speciation Sampler (for elemental and EC/OC analysis)	<2.5 μm	RAAS 2.5 - 400	1	24 hr	12 months
Size Segregated Aerosol	<0.3 to 10 μm	3 Stage RDI	1	24 hr	12 months
Highly-Size Resolved Aerosol	<0.069 to 10 µm	3 Stage RDI	1	24 hr hrly resolution	12 months
PM2.5 for Cytokine/ROS assays	<2.5 μm	UMHFAS	1	1 hr	12 months
Bulk PM	<2.5 μm	UMUHVS	1	1 week	12 months
Organic Compounds	<2.5 μm	2-HP HVS	1	24 hr	12 months
organic compounds	<2.5 μm	- ··· ··· ·	1	1 to 2 hrs	Intensives

Fresno Supersite Phases 2 and 3

Project Summary: This project enhances and extends monitoring at the existing Fresno Supersite such that a continuous record of advanced air quality measurements is available from May 15, 1999 through March 31, 2003. Fresno is one of two prototype Supersites that were initiated during 1999 with Phase 1 measurements acquired until March 31, 2001. The observables and duration for the Phase 1 period are insufficient to support health studies planned for California. Phase 2 will enhance the measurements begun in Phase 1 to accommodate the needs of simultaneous health-related studies in the Fresno area. Phase 3 will extend monitoring through March 31, 2003 and will fully integrate Fresno Supersite measurements with those from other Supersites and with simultaneous health-related studies.

Objectives: Phase 2 and 3 objectives are: 1) test and evaluate non-routine monitoring methods, with the intent to establish their comparability with existing methods and determine their applicability to air quality planning, exposure assessment, and health impact determination; 2) increase the knowledge base of aerosol characteristics, behavior, and sources so regulatory agencies can develop standards and strategies that protect public health; and 3) acquire measurements that can be used to evaluate relationships between aerosol properties, co-factors, and observed health end-points.

Hypotheses: Phases 2 and 3 hypotheses require a multi-year data set that includes large extremes in meteorology, aerosol composition, and emissions. Objective 1 hypotheses are: 1) PM_{2.5} and PM₁₀ measurements by different methods are comparable; 2) mass from number count equals gravimetric mass; 3) hourly coarse particle concentrations can be reliably determined from continuous PM₁₀ and PM_{2.5} measurements; 4) bioaerosols and endotoxins constitute a constant fraction of coarse particle mass; 5) photoionization measurements are correlated with organic particle concentrations; and 6) chemiluminescent NO₂ is equivalent to true NO₂. Objective 2 hypotheses are: 1) statistical aggregates of particle indicators for a single year deviate by less than sampling error from a three-year distribution; 2) continuous carbon measurements differentiate carbon sources from each other; 3) statistical indicators of source contributions do not significantly vary from year to year; 4) particle size, number, surface area, and major chemical component indictors are highly correlated and are equivalent indicators of health risk; and 5) PM_{2.5} and PM₁₀ mass concentrations were higher during drought years than in years with normal precipitation. Objective 3 hypotheses are: 1) respiratory and cardiovascular distress are related to PM_{2.5} concentrations and other indicators; 2) concentration thresholds exist for air quality indicator relationships to health effects; 3) particle characteristics have different effects on the onset and severity of short-term reductions in lung function, asthma attacks, and cardiovascular ailments; 4) animals react differently to different particle size, surface area, chemical, and mass characteristics; and 5) particles in human lungs are similar to those in urban air. Objective 3 hypotheses are to be tested in concurrent epidemiological, toxicological, exposure, and clinical studies that will use Fresno measurements in real time to conduct experiments and retrospectively to analyze the results.

Approach: Supersite observables include in *situ*, continuous, short duration (one hour or less) measurements of: 1) $PM_{2.5}$, PM_{10} , and coarse (PM_{10} minus $PM_{2.5}$) mass; 2) $PM_{2.5}$ sulfate, nitrate, carbon, light absorption, and light extinction; 3) numbers of particles in discrete size bins ranging from 0.01 to ~10 µm; 4) criteria pollutant gases (O_3 , CO, NO_x); 5) reactive gases (NO_y , NO_2 , HNO_3 , NH_3); and 6) single particle characterization by time of flight mass spectrometry. Field sampling and

laboratory analysis are applied for: 1) gaseous and particulate organic compounds (light hydrocarbons, heavy hydrocarbons, carbonyls, polycyclic aromatic hydrocarbons [PAH] and other semi-volatiles); and 2) PM_{2.5} mass, elements, ions, and carbon. Observables common to other Supersites, including: 1) daily PM_{2.5} 24-hour average mass with Federal Reference Method (FRM) samplers; 2) continuous hourly and five minute average PM_{2.5} and PM₁₀ mass with Beta Attenuation Monitors (BAM) and Tapered Element Oscillating Microbalances (TEOM); 3) daily PM_{2.5} chemical speciation with an EPA speciation monitor and protocol; 4) coarse particle mass by dichotomous sampler and difference between PM₁₀ and PM_{2.5} BAM and TEOM measurements; 5) coarse particle chemical composition; and 6) high sensitivity and time resolution scalar and vector wind speed, wind direction, temperature, relative humidity, barometric pressure, and solar radiation. Three satellite sites are operated next to a nearby heavily traveled roadway, in a nearby neighborhood that is influenced by wintertime wood burning, and in a non-urban area south of the Fresno city limits. These sites will evaluate deviations in Supersite measurements owing to source proximity and isolation from urban emitters. Satellite sites are equipped with nephelometers operating continuously and with Minivol Teflon and Quartz filter samplers operating for 24-hours every 6th day to quantify mass, elemental, ion, and carbon concentrations. Data analysis activities have been defined that relate every set of measurements to the hypotheses that will be tested.

Expected Results: 1) a long-term record of simultaneous advanced particle measurements that includes a large range of concentration levels, particle sizes, and aerosol compositions, suitable for many purposes; 2) supportable conclusions about specific hypotheses concerning measurement method performance, causes of excessive pollution levels, and effects on health; 3) continuing linkages and collaboration among air quality scientists, toxicologists, epidemiologists, exposure specialists, and clinicians that better integrate and communicate their scientific findings; 4) a research infrastructure in California that can serve research needs after Supersite monitoring is completed; and 5) peer-reviewed, scientifically sound publications that support local, state, and national decision-making related to standard setting and pollution controls.

Leveraging: The California Air Resources Board has committed substantial support for site operation, quality auditing, and data management. Planned and pending health studies using Supersite data include: 1) Particulate Air Pollution and the Natural History of Childhood Asthma; 2) Particulate Air Pollution and the Natural History of Adult Asthma; 3) Estimating Indoor Exposure from Ambient Concentrations; 4) Health Effects of Concentrated Ambient Particles from the Central Valley of California; and 5) Relationships Among Air Quality Indicators and Medical Health Records. These projects have certain or pending support from the Air Resources Board, Department of Energy, the U.S. EPA, and other sources.

Supplemental Keywords: $PM_{2.5}$, PM_{10} , PM HEALTH EFFECTS, ULTRAFINE, CONTINUOUS AEROSOL MONITOR

Table 1. Observables, measurement methods, sample durations, frequencies and monitoring periods for the Fresno Supersite.

Observable and Method	Size Range	Avg Time	Frequency	Period
Gases				
NO/NO _x (TEI 42 chemiluminescence) ^c	gas	1-hr	daily	1990 onward ^a
Ozone (API 400 UV absorption) ^c	gas	1-hr	daily	1990 onward ^a
Carbon monoxide (Dasibi 3008 infrared absorption)	gas	1-hr	daily	1990 onward ^a
Non-methane hydrocarbons	gas	1-hr	daily	1990 onward ^a
$\mathrm{NO_{y}}$ (high sensitivity TEI 42 with external converters and denuders) ^c	gas	5-min	daily	12/15/99 to 3/31/03
HNO ₃ (high sensitivity TEI 42 or Ecophysics chemiluminescent monitor with external converters, denuders & sequencers) ^d	gas	5-min	daily	12/1/00 to 3/31/03
Ammonia (TEI 17C high sensitivity with NO _x scrubbers and oxidizers) ^d	gas	5-min	daily	12/1/00 to 3/31/03
Filter Mass and Chemistry				
TSP mass (hivol w/ quartz filters) and lead	TSP	24-hr	12th day	1990 onward ^a
PM_{10} mass, sulfate, nitrate, chloride, and ammonium (hivol SSI w/ quartz filters)	0 to 10 μm	24-hr	6th day	1990 onward ^a
PM _{2.5} and coarse mass, elements (dichotomous samplers with Teflon filters)	0 to 2.5 μm 0 to 10 μm	24-hr	6th day	1990-11/1/00 a
PM _{2.5} and coarse mass, elements. Coarse endotoxins, spores, molds, fungi (dichotomous samplers with Teflon filters)	0 to 2.5 μm 0 to 10 μm	24-hr	every day	11/1/00-12/3/05 a,e
PM _{2.5} mass (collocated Andersen sequential FRM w/ Teflon filters)	0 to 2.5 μm	24-hr	daily for primary 6th day collocated	3/1/99 onward ^a
PM _{2.5} mass, light absorption, elements, ions, and carbon (two single-channel FRMs w/ Teflon and quartz filters)	0 to 2.5 μm	24-hr	6th day	7/5/99 to 6/29/00 (method evaluation)
PM _{2.5} mass, elements, ions, and carbon (six-channel Andersen RAAS speciation sampler w/ denuders and backup filters)	0 to 2.5 μm	24-hr	6th day	7/5/99 to 6/29/00 (method evaluation)
Particle morphology (Airmetrics Minivol w/ polycarbonate filters and scanning electron microscopy)	0 to ~30 μm	24-hr	6th day	7/5/99 to 6/29/00 (method evaluation)
PM _{2.5} mass, elements, ions, and carbon (two-channel speciation sampler)	0 to 2.5 μm	24-hr	3 rd day	2001 onward ^a
PM _{2.5} mass, elements, ions, volatilized nitrate, carbon, and ammonia at three neighborhood (satellite) sites (six Airmetrics MiniVols w/ Teflon/citric acid cellulose and quartz/NaCl cellulose filter packs)	0 to 2.5 μm	24-hr	6th day	12/1/99 to 3/31/03

 Table 1. (continued)

Observable and Method	Size Range	Avg Time	Frequency	Period
Filter Mass and Chemistry (continued)				
PM _{2.5} mass, elements, ions, carbon, and ammonia (two-channel sequential filter sampler w/ denuders and backup filters; mass on all, chemistry on 100 samples) ^c	0 to 2.5 μm	24-hr	daily	12/1/99 to 1/31/01 ^b
${ m PM}_{2.5}$ mass, elements, ions, and carbon (two-channel sequential filter sampler w/ denuders and backup filters) $^{\rm c}$	0 to 2.5 μm	3-, 5-, and 8-hr 5/day	daily on episode days	15 episode days 12/1/00 to 1/31/01 ^b
${ m PM}_{10}$ mass, elements, ions, carbon, and fugitive dust markers (methods to be specified by CRPAQS) $^{ m c}$	0 to 10 μm	24-hr	daily sampling with selected characterization	9/15/00 to 11/15/00 ^b
Toxic species (metals, chromium VI, aldehydes) (Xontec 920)	0 to ~30 μm	24-hr	12th day	1996 onward ^a
Continuous Particle Mass and Chemistry				
PM _{2.5} mass (30 °C TEOM)	0 to 2.5 μm	1-hr	daily	7/5/99 to 3/31/03
PM ₁₀ mass (30 °C TEOM)	0 to 10 μm	1-hr	daily	7/5/99 to 3/31/03
PM _{2.5} mass (ambient temperature BAM) ^c	0 to 2.5 μm	1-hr	daily	5/15/99 onward ^a
PM ₁₀ mass (ambient temperature BAM) ^c	0 to 10 μm	1-hr	daily	5/15/99 onward ^a
$PM_{2.5}$ nitrate and sulfate (ADI flash volatilization with TEI NO_x detector) ^d	0 to 2.5 μm	10-min	daily	9/23/99 to 3/31/03
$\mathrm{PM}_{2.5}$ nitrate and sulfate (ADI flash volatilization with TEI SO_2 detector) $^\mathrm{d}$	0 to 2.5 μm	10-min	daily	2/1/00 to 3/31/03
PM _{2.5} organic and elemental carbon (R&P Series 5400 carbon monitor) ^c	0 to 2.5 μm	30-min	daily	12/15/99 to 3/31/03
PM _{2.5} organic and elemental carbon (MET ONE in situ analyzer)	0 to 2.5 μm	30-min	daily	4/1/01 to 3/31/03
Individual particle size and chemistry (UC Riverside time-of-flight spectrometer)	0 to 10 μm	5-min	daily on episode days	15 episode days 12/1/00 to 1/31/01 b
Organic Gases and Particles				
Toxic hydrocarbons (Xontec 910 canister sampler)	gas	24-hr	12th day	1995 onward
Carbonyls (Xontec 925 DNPH sampler) ^c	gas	24-hr summer 4/day	12th day 3rd day	1995 onward ^a 1995 onward ^a
Light hydrocarbons (canister & GC/FID) ^c	gas	5- to 8-hr, 4/day	daily for episodes	15 episode days 12/1/00 to 1/31/01 b
Organic Gases and Particles (continued)				
Heavy hydrocarbons (TENAX & GC/TSD/FID) ^c	gas	5- to 8-hr, 4/day	daily for episodes	15 episode days 12/1/00 to 1/31/01 b
Aldehydes (DNPH & HPLC) °	gas	5- to 8-hr, 4/day	daily for episodes	15 episode days 12/1/00 to 1/31/01 b
PM _{2.5} organic compounds (Teflon-coated glass-fiber/PUF/XAD filters and GCMS) ^c	0 to 2.5 μm	5- to 8-hr, 4/day	daily for episodes	15 episode days 12/1/00 to 1/31/01 b

Observable and Method	Size Range	Avg Time	Frequency	Period
PM _{2.5} organic compounds (Teflon-coated glass-fiber/PUF/XAD filters and GCMS)	0 to 2.5 μm	24-hr	6th day	6/1/00-9/30/00 ^b
PM _{2.5} organic compounds (Minivol w/ Teflon-coated glass-fiber filters and GCMS) (aggregated for 60 sample polycyclic aromatic hydrocarbon [PAH] analysis) ^c	0 to 2.5 μm	24-hr	6th day	2/1/00 to 1/31/01 ^b
Continuous particle-bound PAHs (EcoChem Analytics PAS2000 w/ UV radiation and photoelectric aerosol sensors)	0 to 1 μm	5-min	daily	9/30/99 to 3/31/03
Continuous Light Scattering				
Ambient particle light scattering (Optec NGN2 ambient-temperature nephelometer at 550 nm)	0 to ~30 μm	5-min	daily	5/15/99 to 3/31/03
Dry particle light scattering (Optec NGN3 heated nephelometer at 550 nm)	0 to 2.5 μm	5-min	daily	5/15/99 to 12/31/99 (method evaluation)
Total particle light scattering (Radiance M903 nephelometer with smart heater at 530 nm) ^c	0 to ~30 μm	5-min	daily	12/15/99 to 3/31/03
PM _{2.5} particle light scattering (Radiance M903 nephelometer with smart heater at 530 nm)	0 to 2.5 μm	5-min	daily	12/15/99 to 3/31/03
Light scattering (TSI- DUSTRACK photometer at 780 nm)	0 to 2.5 μm	5-min	daily	5/15/99 to 3/31/01
Light Absorption				
Coefficient of haze (AISI paper tape sampler)	0 to ~30 μm	2-hr	daily	1990 onward ^a
Light absorption (McGee aethalometer at 880 nm) ^c	0 to 2.5 μm	5-min	daily	5/15/99 to 3/31/03
Light absorption (McGee multi-color [450, 570, 590, 615, 660, 880, and 950 nm] aethalometer)	0 to 2.5 μm	30-min	daily	5/15/99 to 3/31/03
Particle Sizes				
Scanning mobility particle sizer (TSI 3936L10 with 3010S ultrafine condensation particle counter w/ TSI 3080L electrostatic classifier and differential mobility analyzer and TSI 3900087 software) c	10 to 1,000 nm	5-min	daily	12/15/99 to 3/31/03
Particle Sizes (continued)				
Fine particle size distribution in 8 size fractions (0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1.0, and 2.0 µm) (PMS Lasair 1003 optical particle counter) c	0.1 to 2 μm	5-min	daily	11/1/99 to 3/31/03
Aerodynamic particle sizer (TSI 3926)	0.3 to 10 μm	5-min	daily	2/1/01 to 3/31/03
Coarse particle size distribution in 16 size fractions (0.3, 0.4, 0.5, 0.63, 0.8, 1.0, 1.3, 1.6, 2.0, 2.5, 3.2, 4.0, 5.0, 6.3, 8.0, and 10 μ m) (Climet CI-500 optical particle counter) c	0.5 to 10 μm	5-min	daily	12/15/99 to 3/31/03

Observable and Method	Size Range	Avg Time	Frequency	Period
Mass and ion size distribution in 9 size fractions (0.054, 0.105, 0.148, 0.37, 0.54, 1.0, 1.8, 3.2, 5.6, and 15 μ m) (MOUDI with Teflon filters and IC and AC)	0.054 to 15 μm	5- to 8-hr	daily for episodes	15 Episode Days 12/1/00-1/31/01 ^b
Carbon size distribution in 9 size fractions (0.054, 0.105, 0.148, 0.37, 0.54, 1.0, 1.8, 3.2, 5.6, and 15 μm) (MOUDI with aluminum filters and TOR)	0.054 to 15 μm	5- to 8-hr	daily for episodes	15 Episode Days 12/1/00-1/31/01 ^b
Meteorology				
Wind speed/direction (Met One 05305L high-sensitivity wind vane and anemometer) ^c	NA	5-min	daily	5/15/99 onward ^b
Temperature (Met One CS500L high-accuracy sensor) ^c	NA	5-min	daily	5/15/99 onward ^b
Relative humidity (Met One CS500L high-accuracy sensor) ^c	NA	5-min	daily	5/15/99 onward ^b
Solar radiation (Met One LI200X-L) °	NA	5-min	daily	9/15/99 onward ^b
Barometric pressure sensor ^c	NA	5-min	daily	9/15/99 onward ^b
Data Acquisition and Processing				
Campbell Scientific 24-input analogue data logger with modem dialup	NA	All times	daily	5/15/99 onward ^b
PC-LABVIEW serial data logger with modern dialup ^c	NA	All times	daily	12/1/99 onward ^b

Table 1. (continued).

- ^a Part of the California Air Resources Board's compliance monitoring network.
- Measurements from the California Regional Particulate Air Quality Study (CRPAQS) (Watson et al., 1998a). Three to five wintertime episodes of four to eight day duration will be monitored based on a forecast of high PM_{2.5} concentrations under clear sky stagnation and stagnation with fog conditions.
- ^c These ground-level measurements will also be taken at the non-urban Angiola site established by CRPAQS from 2/1/00 through 1/31/01 and during pollution episodes. This site is located 100 km south of Fresno in a flat area of the San Joaquin Valley surrounded by agricultural fields dominated by cotton and alfalfa. Simultaneous measurements from Angiola will be used with those from the Fresno site to evaluate hypotheses about measurement equivalence in the absence of fresh urban emissions and to separate urban from non-urban contributions to the concentrations of measured observables. CRPAQS episodic measurements at Angiola will be taken at the same time as those acquired at Fresno.
- ^d Measurements at Angiola are available from 12/1/00 through 1/31/01.
- ^e Part of Particulate Air Pollution and the Natural History of Childhood Asthma sponsored by ARB.

C.ABSTRACT

Sorting Code: Particulate Matter "Supersites" Program, 99-NCERQA-X1 **Title:** Gulf Coast Aerosol Research and Characterization Program (GC-ARCH)

Principal Investigator: David Allen, The University of Texas at Austin

Co-Principal Investigator: Matthew Fraser, Rice University

Co-investigators: D. Collins, Texas A&M; S. Dasgupta, Texas Tech; S. Hering, Aerosol Dynamics; P. Hopke, Clarkson University; A. Russell, Georgia Tech; A. Wexler, University of

Delaware

Collaborating institutions: Brookhaven National Laboratory, City of Houston, Houston Regional Monitoring Network, Mickey Leland National Urban Air Toxics Research Center, NOAA, Texas Hazardous Substance Research Center, Texas Natural Resource Conservation Commission, Southern California Center for Airborne Particulate Matter, Southern Oxidants Study, University of Texas Houston Health Science Center

Lead Institutions: The University of Texas at Austin, Rice University

Project Period: 12/1/99 - 9/30/03

Project Cost: Project Summary:

A fine particulate matter (fine PM) "Supersite" for Southeastern Texas is proposed. This Supersite would be located in a region where approximately 2.5 million people may be exposed to annual average PM concentrations in excess of $15 \,\mu \text{g/m}^3$. Significant fine PM exposures are not the only rationale, however, for choosing Southeastern Texas as a location for a PM Supersite. The Houston area is home to the largest concentration of petrochemical manufacturing facilities in the United States, and as a consequence the industrial source signatures for PM and PM precursors are strong, particularly for organics. Emissions from typical urban anthropogenic sources and biogenic sources are also significant. Finally, exposure studies, toxicological studies, and a large ambient air quality field study are planned for the summer of 2000 in Southeastern Texas. These studies will provide valuable data sets that can be combined with the data to be collected by the program described in this proposal.

Objectives: The specific objectives of the research program described in this proposal will be

- 1. to collect physicochemical data on fine PM that can be used to characterize spatial and temporal variability in fine PM source contributions and composition, in Southeastern Texas
- 2. to characterize spatial and temporal variability in fine PM source contributions and composition, throughout the southeastern United States, and
- 3. to examine the physical and chemical process that govern PM formation and transformation in Southeastern Texas

Three additional objectives will be addressed by integrating the measurements made in this program with measurements to be made in separately funded studies. These objectives will be:

- 4. to develop a combined database on PM, gas phase air pollutants and meteorological variables, suitable for testing models of the formation and fate of fine PM; this objective will be achieved by coordinating with a large, integrated ozone and PM field study planned by the Southern Oxidants Study
- to examine exposures to fine PM from specific source categories in Southeastern Texas; this objective
 will be achieved by coordinating with an exposure study currently underway in Houston, funded by the
 Mickey Leland National Urban Air Toxics Research Center, and

6. to relate the physicochemical data on fine particulate matter to mammalian cell responses; this objective will be achieved by coordinating with an EPA funded project currently underway at the University of Texas Houston Health Science Center.

Approach: The proposed measurements would be made at 3 core sites. The core sites will be tied to approximately 20 peripheral, fine PM monitoring sites operated by the Texas Natural Resource Conservation Commission and other organizations. Measurements will be made over a 16 month period, beginning in June, 2000. To maximize leveraging opportunities, a 6 week intensive sampling program, during August and September 2000, will be embedded in the 16 month field program. The specific measurements to be made, and the relationship of the measurements to the study objectives, are described in detail in the proposal.

Expected Results: The three primary objectives of the Supersites program, as described in the Request for Applications, are to characterize particulate matter and its sources, support health effects and exposure research, and to conduct methods testing. The proposed program will address each of these program goals and will test a number of scientific hypotheses.

Characterizing particulate matter and its sources: Spatial and temporal variability in fine PM source contributions and composition will be assessed in Southeastern Texas and throughout the Southeastern United States. In addition, the chemical and physical processes that control fine PM formation in regions with substantial emissions of organics will be examined. Some of the hypotheses that will be examined are (a more complete list is given in the proposal):

- Source profiles of PM in Southeastern Texas are substantially different than those in the Southeastern U.S. east of the Mississippi River. Spatial gradients in fine PM concentrations and composition are greater in the Houston area than in Atlanta and other southern cities. Maximum fine PM concentrations are observed in the summer, when secondary PM generation peaks.
- Variations in fine PM concentration and composition on a 10-15 minute time scale are substantial and this temporal variability will be related to variability in ozone concentrations.
- Rates of condensation of organics onto hydrophobic and hydrophilic PM are different, and the condensation rates depend on the hydrophobic surface area available for condensation.
- Rates of PM growth are correlated with concentrations of semivolatiles, peroxides, and acid gases and gas/particle partitioning ratios for organics depend on the hydrophobic surface area available for condensation.

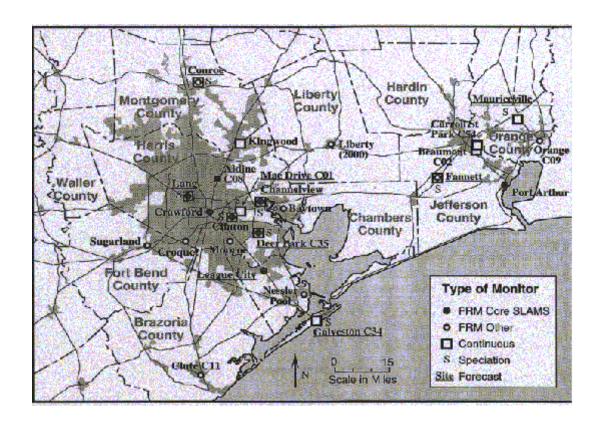
Collaboration with investigators performing PM exposure and toxicology studies will allow the following hypotheses related to *health effects and exposure* to be examined:

- PM characteristics measured at ambient air quality sites can be different than ambient concentrations outside of homes, and the relationship depends on the land cover surrounding the homes.
- Source strengths for fine PM indoors and outdoors differ, and indoor penetration of PM in hot and humid climates is a strong function of PM size.
- Human alveolar macrophage response depends on source contributions and PM composition. Finally, *methods testing*, and evaluation of different methods of characterizing PM will be quantitatively examined in both the 6 week and 16 month programs.

Supplemental Keywords: air; fine particulate matter, measurement methods; EPA Region 6; Texas

1. Map of Core and Peripheral PM monitoring sites.

A dot on a site indicates that the Federal Reference Method sampler for fine PM will be operated at the site. An S indicates that speciation measurements (trace metals, inorganic ions and organic/elemental carbon) will be made. The core sites are a privately operated site (HRM Site #3) near Clinton, Deer Park, and Aldine.



2a. MEASUREMENTS to be made at the core sites

Measurement	Houston Regional	Deer Park (upwind	Aldine (downwind
	Monitoring (HRM)	industrial)	urban)
	Network Site 3	·	,
PM	(downwind industrial)		
I IVI			
measurements			
Federal Reference	Every sixth day PM ₁₀ and	Every third day PM ₁₀ and	Every third day PM ₁₀ and
Method (FRM)	PM _{2.5} (HRM)	PM _{2.5} (TNRCC)	PM _{2.5} (TNRCC)
Continuous PM Mass	HRM	TNRCC	TNRCC
(TEOM)			
Inorganic ions	Every third day at nearby	Every third day (TNRCC)	Every third day (TNRCC)
	TNRCC site (TNRCC)		
OC/EC	Every third day at nearby	Every third day (TNRCC)	Every third day (TNRCC)
	TNRCC site (TNRCC)		
Trace metals	Every third day at nearby	Every third day (TNRCC)	Every third day (TNRCC)
	TNRCC site (TNRCC)		, , , , , , , , , , , , , , , , , , , ,
Near real time sulfate	HRM using Aerosol	Aerosol Dynamics,	Aerosol Dynamics,
Tear tear time surface	_	•	
NI 14'	Dynamics instrument	(ADI)-GCARCH	(ADI)-GCARCH
Near real time nitrate Near real time	HRM	ADI -GCARCH ADI -GCARCH	ADI-GCARCH ADI –GCARCH
	ITKW	ADI -GCARCII	ADI –GCARCII
carbon			
Molecular	Selected dates from filter	Selected dates from filter	Selected dates from filter
characterization of	samples collected every	samples collected every	samples collected every
organic fractions	third day (Rice-	third day (Rice-	third day (Rice-
	GCARCH)	GCARCH)	GCARCH)
Gas measurements			
Ozone, CO	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO, NO _x	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO_{v}		Continuous (TNRCC)	Continuous (TNRCC)
Denuder HNO ₃	Third day (Rice-	Third day (Rice-	Third day (Rice-
	GCARCH)	GCARCH)	GCARCH)
Denuder NH ₃	Third day (Rice-	Third day (Rice-	Third day (Rice-
	GCARCH)	GCARCH)	GCARCH)
SO_2	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)

PAMS hydrocarbons	Auto-GC (HRM)	Auto-GC (TNRCC)	Canister (UT-GCARCH)
Carbonyls	On forecast (HRM)	Third day (TNRCC)	Third day (Rice-
			GCARCH)
Met. Data*	HRM	TNRCC	TNRCC

^{*}Meteorological data includes wind speed, wind direction, relative humidity and solar radiation

2b. METHODS to be used at the core sites

	Measurement	Method
	PM measurements	
1	Federal Reference Method (FRM)	Standard Reference Method
2	Continuous PM Mass (TEOM)	
3	Inorganic ions	EPA Speciation Network
4	OC/EC	EPA Speciation Network
5	Trace metals	EPA Speciation Network
6	Near real time sulfate	Method of Stolzenburg & Hering (1998, 1999)
7	Near real time nitrate	Method of Stolzenburg & Hering (1998, 1999)
8	Near real time carbon	Method of Stolzenburg & Hering (1998, 1999)
9	Molecular characterization of organic fractions	Gas chromatography/mass spectometry
	Gas measurements	
10	Ozone, CO	CAMS method
11	NO, NO _x	CAMS method
12	NO_y	CAMS method
13	Denuder HNO ₃	Ion chromatography
14	Denuder NH ₃	Ion chromatography
15	SO_2	CAMS method
16	PAMS hydrocarbons	-Gas chromatographs (Auto-GC)
		-Cryofocussed and analyzed by gas
		chromatography with flame ionization
		detection (US.EPA, 1989)
		-Canister sampling.
17	Carbonyls	2,4-dinitrophenyl-hydrazine (DNPH) sampling
		techniques
18	Met. Data*	CAMS method

^{*}Meteorological data includes wind speed, wind direction, relative humidity and solar radiation

3a. Particulate Phase measurements to be performed at core sites during 6 week intensive

Measurement	HRM Site #3	Deer Park /LaPorte	Aldine (downwind
	(downwind industrial)	(upwind industrial)	urban)
Particulate matter			
measurements			
FRM	Every sixth day PM ₁₀	Every third day PM ₁₀	Every third day PM ₁₀
	and PM $_{2.5}$ (HRM),	and PM _{2.5} (TNRCC)	and PM $_{2.5}$ (TNRCC)
	Daily at nearby TNRCC		
	site (TNRCC)		
Continuous PM Mass	HRM	TNRCC	TNRCC
Inorganic ions	Every third day at	Every third day	Every third day
	nearby TNRCC site	(TNRCC)	(TNRCC)
	(TNRCC)		
OC/EC	Every third day at	Every third day	Every third day
	nearby TNRCC site	(TNRCC)	(TNRCC)
	(TNRCC)	T 41:11	T. 41.1.1
Trace metals	Every third day at	Every third day	Every third day
	nearby TNRCC site	(TNRCC)	(TNRCC)
Near real time sulfate	(TNRCC) HRM using Aerosol	Aerosol Dynamics,	A area al Demanica
Near rear time surrate	Dynamics instrument,	(ADI)-GCARCH	Aerosol Dynamics, (ADI)-GCARCH
	Texas Tech instrument	(ADI)-GCARCII	(ADI)-GCARCH
Near real time nitrate	Texas Tech Instrument	ADI -GCARCH	ADI-GCARCH
Near real time carbon	HRM	ADI -GCARCH	ADI –GCARCH
Molecular characterization	Selected dates from	Selected dates from	Selected dates from
of organic fractions	filter samples collected	filter samples collected	filter samples collected
or organic fractions	every third day (Rice-	every third day (Rice-	every third day (Rice-
	GCARCH)	GCARCH)	GCARCH)
Size distributions	GC-ARCH	ADI -GCARCH	,
Single particle MS	Univ. Del. (GC-ARCH)		
Organic compound classes	Daily	Daily	Daily
of size resolved PM	(UT-GCARCH)	(UT-GCARCH)	(UT-GCARCH)
Additional PM	Year 2000 Field Study	Year 2000 Field Study	Year 2000 Field Study
measurements, ground			
based and aircraft			

3b. Particulate phase Methods to be performed at core sites during 6-week intensive.

	Measurement	Method
	Particulate matter measurements	
1	FRM	Standard Reference Method
2	Continuous PM Mass	
3	Inorganic ions	EPA speciation
4	OC/EC	EPA speciation
5	Trace metals	EPA speciation
6	Near real time sulfate	Method of Stolzenburg & Hering (1998, 1999)
7	Near real time nitrate	Method of Stolzenburg & Hering (1998, 1999)
8	Near real time carbon	Method of Stolzenburg & Hering (1998, 1999)
9	Molecular characterization of organic fractions	Gas chromatography/mass spectometry
	Size distributions	DMA/CNC
10	Single particle MS	University of Delaware
11	Organic compound classes of size resolved PM	Low Pressure Impactor/FTIR
12	Additional PM measurements, ground based and aircraft	See attachments

3c. Gas phase measurements to be performed at core sites during 6 week intensive

Measurement	HRM Site #3	Deer Park /LaPorte	Aldine (downwind
	(downwind industrial)	(upwind industrial)	urban)
Gas phase			
measurements			
Ozone, CO	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO, NO _x	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
NO_y		Continuous (TNRCC)	Continuous (TNRCC)
Denuder HNO ₃	Third day	Third day	Third day
	(Rice-GCARCH)	(Rice)	(Rice)
Denuder NH ₃	Third day	Third day	Third day
	(Rice-GCARCH)	(Rice-GCARCH)	(Rice-GCARCH)
Acid gases: SO ₂ , HCl,		Semi-continuous	
HONO, HNO ₃		(TTU-GCARCH)	
NH_3		Semi-continuous	
		(TTU-GCARCH)	
SO_2	Continuous (HRM)	Continuous (TNRCC)	Continuous (TNRCC)
PAMS hydrocarbons	Auto-GC	Auto-GC	Canister
	(HRM)	(TNRCC)	(UT-GCARCH)
Carbonyls	Selected dates	Selected dates from	Selected dates from
	(HRM)	samples collected daily	samples collected daily
		by TNRCC	by TNRCC
		(TNRCC)	(Rice-GCARCH)
Semi-volatiles		Selected dates from	
		samples collected daily	
		by EPA	
Peroxides		Semi-continuous	
		(TTU-GCARCH)	
Additional gas phase	Year 2000 Field Study	Year 2000 Field Study	Year 2000 Field Study
measurements, ground			
based and aircraft			
Met. Data	TNRCC	TNRCC	TNRCC

^{*}Meteorological data includes wind speed, wind direction, relative humidity and solar radiation

3d. Gas phase methods to be used at the core sites during 6-week intensive

Measurement	Method	See Project Description
Gas phase measurements		
Ozone, CO		
NO, NO _x		
NO_v		
Denuder HNO ₃		
Denuder NH ₃		
Acid gases: SO ₂ , HCl, HONO,		
HNO_3		
NH ₃		
SO_2		
PAMS hydrocarbons		
Carbonyls		
Semi-volatiles		
Peroxides		
Additional gas phase		
measurements, ground based		
and aircraft		
Met. Data		

^{*}Meteorological data includes wind speed, wind direction, relative humidity and solar radiation

4. Data to be collected at peripheral sites (all data to be collected by the TNRCC)

Site	FRM	TEOM	Inorganic	Trace Metals	OC/EC	Met.
			Ions			Data*
Aldine	Daily					X
Baytown	Every sixth day					X
Channelview	Daily	X	X	X	X	X
Clinton	Daily	X	X	X	X	X
Clute	Every sixth day					X
Conroe	Every third day	X	X	X	X	X
Crawford	Every third day					X
Croquet	Every sixth day					X
Galveston						X
Kingwood		X				X
League City	Every third day					X
Liberty	Every sixth day					X
Mae Drive		X	X	X	X	X
Monroe	Every sixth day					X
Nessler Pool	Every sixth day					X
Sugarland	Every sixth day					X
Beaumont		X				X
Carroll St.		X				X
Park						
Fannett	Every third day	X	X	X	X	X
Mauriceville		X	X	X	X	X
Orange	Every sixth day					X
Port Arthur	Daily					X

^{*}Meteorological data includes wind speed and wind direction at all sites and relative humidity and solar radiation at selected sites

C. ABSTRACT

- **C.1** Research Category and Sorting Code: Particulate Matter "Supersites" Program, 99-NCERQA-X1
- **C.2 Title:** Southern California Particulate Matter Supersite (SCPMS)
- C.3 Investigators: Principal Investigator John R. Froines Ph.D., Professor, Environmental Health Sciences, UCLA. Co-Principal Investigators William C. Hinds, Sc.D., Professor, Environmental Health Sciences, UCLA, Constantinos Sioutas, Sc.D., Assistant Professor, Environmental Engineering, University of Southern California. Other Investigators California Institute of Technology: Glen R. Cass, Ph.D., Research Scientist, Environmental Engineering. UCLA: Arthur K. Cho, Ph.D., Professor Emeritus, Pharmacology, Sheldon K. Friedlander, Ph.D., Parsons Professor, Chemical Engineering, Antonio H. Miguel, Ph.D., Principal Development Engineer, Institute of the Environment. University of California, Riverside: Janet Arey, Ph.D., Professor, Environmental Sciences and Environmental Sciences and Environmental Toxicology. University of Southern California: Edward L. Avol, Associate Professor, Occupational and Environmental Health.
- **C.4 Institutions:** University of California, Los Angeles (Los Angeles, CA) lead campus, California Institute of Technology (Pasadena, CA), University of California, Riverside (Riverside, CA), University of Southern California (Los Angeles, CA).
- **C.5 Project Period:** January 1, 2000 December 31, 2004

C.6 Project Cost: \$3,499,908

C.7 Project Summary:

The overall objective of the Southern California Particle Matter Supersite (SCPMS) is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution chemical composition and physical state, spatial and temporal variability and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). The research objectives of the Southern California Particulate Matter Supersite are:

- 1. To characterize PM, its constituents and precursors, to better understand sources and transport affecting human exposure and to support development of State Implementation Plans (SIPs).
- 2. To obtain atmospheric measurements to support health studies designed to address causal factors; etiologic pathways and mechanisms of PM related morbidity and mortality with particular emphasis on PM source-receptor-exposure-effects pathways.

3. To conduct methods testing that will enable comparisons and evaluation of different technologies for characterizing PM including evaluation of new instrumentation, sampling methods and federal reference methods.

The LAB is home to more than 15 million individuals and it has been described as the most polluted airshed in the nation, with a complex, persistent and unique airborne particulate matter. Despite considerable improvements in air quality over the past two decades, Los Angeles continues to exhibit the most severe ozone and PM air quality problem in the U.S. Los Angeles should be studied as a region by itself because it epitomizes a noticeable and yet distinct fine particle air quality problem in terms of particle composition, source mix, and meteorology. These factors represent important considerations for Supersite location and they indicate that Southern California is a particularly important environment and opportunity for additional studies. The proposed SCPMS activities will be integrated with the multidisciplinary research in exposure assessment, toxicology, and epidemiology of the recently funded by the EPA STAR Southern California Center for Airborne Particulate Matter (SCCAPM). The SCPMS will interact with the California Air Resources Board (ARB) and the South Coast Air Quality Management District (SCAQMD) to maximize the use and value of the data collected by the SCPMS and the State and Local Agencies on PM. The monitoring activities of the SCPMS will be also linked with toxicology studies in the LAB using a mobile PM concentrator facility to investigate health effects associated with exposures to ultrafine, fine and coarse particles. These studies are funded by the SCCAPM, the Health Effects Institute (HEI), the ARB and the National Institute of Environmental Health Sciences (NIEHS). The SCPMS will therefore become an invaluable resource to the major ongoing and planned PM health and modeling studies in the LAB.

Specific projects in the category of PM Characterization provide the information that is needed to understand the relationship between PM sources and receptors, as well as providing insight into the factors that affect the spatial and temporal variability of PM characteristics. These projects are: 1) Comprehensive characterization of Particulate Matter in the LAB and correlations between particle size distribution, chemical composition and gaseous co-pollutants; 2) Determination of the occurrence, frequency and prevalence of PM_{2.5} sub-modes in different locations of the LAB; 3) Systematic evaluation of sampling artifacts of the Federal Register Method (FRM) in measuring PM_{2.5}, PM₁₀ and Coarse PM concentrations; 4) Study of PM formation and growth mechanisms in different locations of the LAB; 5) Testing of the hypothesis of that 2.5 µm represents a clear cutpoint between coarse and fine PM and does not depend on location or season; 6) Determination of the seasonal and spatial variation of ultrafine, accumulation and coarse PM in the LAB and their relation to sources. These studies will be conducted in collaboration with AQMD and ARB; 7) Comparison between the true PM2.5, PM₁₀ and coarse PM concentrations with those determined gravimetrically with a FRM and evaluate sampling artifacts related to the loss of volatile or semi-volatile PM compounds.

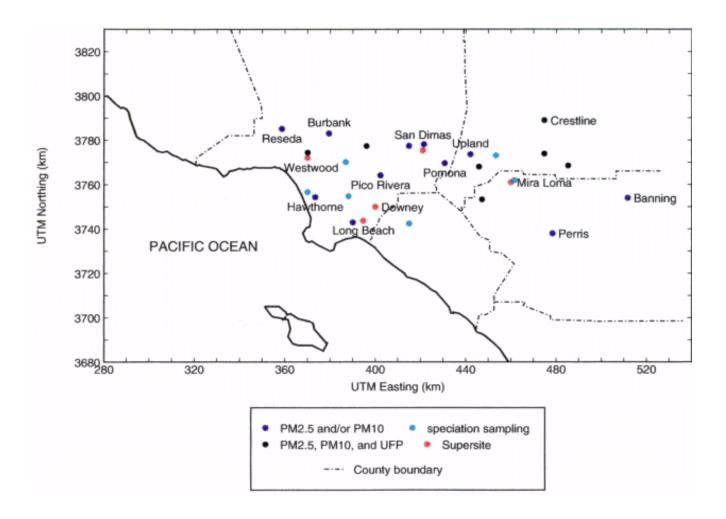
Projects in the category of Support of Health Effects and Exposure Research are: 1) Detailed physico-chemical characterization of concentrated PM used in ongoing toxicity studies currently under way in the LAB; 2) Measurement of within-community PM variability for improved dispersion models describing personal exposure indices based on traffic-based emissions for use in ongoing epidemiological investigations of chronic respiratory health effects of ambient particle matter in children; 3) Measurement of the size distribution as well as the spatial and seasonal variation of particle bound PAH, oxy-PAH, nitro-PAH, quinones and other polar PAHs in the LAB; 4) Determination of the contribution of volatile and semi-volatile species to Total Suspended $PM_{2.5}$ mass and assess any resulting bias in interpreting epidemiological results; 5) Measurement of aerosol oxidant partitioning in the ultrafine, accumulation and coarse PM modes; 6) Analysis of particle-bound PAH and related compounds as a function of distance from freeways; Measurement of protein, allergens and other biological constituents of urban airborne particulate matter.

Projects in the category of Methods Testing are: 1) Comparison between the actual 24-hour averaged PM_{10} and $PM_{2.5}$ concentrations with those determined using continuous PM mass monitors, including the Scanning Mobility Particle Sizer (SMPS), Aerodynamic Particle Sizer (APS), Tapered Element Oscillating Microbalance (TEOM), Continuous Ambient Mass Monitor (CAMM) and the Real-Time Ambient Monitor (RAM); 2) Comparison between the real-time size distribution and mass concentration determined with the SMPS and APS with the 24-hour averaged mass-based size distribution measured with the Microorifice Uniform Deposit Impactor; 3) Development of a semi-continuous monitor for size-dependent nitrate, carbon and sulfate measurement; 4) Evaluation and comparison of new and emerging measurement methods for single-particle analysis.

Intensive aerosol measurements that collect PM data beyond the traditional $PM_{2.5}$ mass, sulfate and nitrate concentrations will be conducted 5 discrete areas of the Los Angeles Basin. These areas will be chosen to provide a wide geographical coverage, and thus to be as representative as possible of human exposures to these pollutants. A mobile Particle Instrumentation Unit (PIU), funded separately by the SCCAPM, will be deployed to these locations to conduct PM measurements. Sampling in each site will last for 6 months and measurements will be repeated on a 2.5-year cycle. During the first of the 6 months, the PIU will be deployed to 5 discrete locations downwind and one location upwind to a freeway close to the central site to determine PM characteristics as a function of freeways distance. A number of existing PM sites operated by AQMD will be used as satellite sites, in addition to the 5 SCPMS sites, to obtain spatial PM variability in the LAB as a function of size and composition.

C.8 Supplemental Keywords: airborne particulate matter, size distribution, PAH, within-community variability, freeways, measurement artifact, diesel exhaust, fine, ultrafine and coarse particulate matter, mobile sources, PM_{2.5}

Selected Supersite Sampling Locations



Equipment for Particle Instrumentation Unit

Monitor	onitor PM Property		Sampling Frequency	
PM Measurements		•	<u> </u>	
Scanning Mobility Particle Sizer (SMPS 3934, TSI Inc.)	Particle number, surface and volume distribution (size range: 0.01–0.7 µm).	15-min	Daily	
Aerodynamic Particle Sizer (APS 3310, TSI Inc.)	Particle number, surface and volume size distribution (size range: 0.5–20 µm).	15-min	Daily	
PM ₁₀ and PM _{2.5} Tapered Element Oscillating Microbalance (TEOM Model 1400, R&P, Inc.)	Continuous measurement of the <i>non-volatile</i> component of ambient PM _{2.5} and PM ₁₀ .	1-hr	Daily	
PM _{2.5} Continuous Ambient Mass Monitor (CAMM; Babich et al, 1999)	continuous PM ₁₀ and PM _{2.5} particulate mass concentrations from the pressure drop across porous membrane filters	1-hr	Daily	
Continuous nitrate, sulfate and carbon monitor (ADI/R&P)	Size-segregated measurement of PM ₁₀ carbon, nitrate and sulfate content	1-hr	Daily	
Real-Time Ambient Mass (RAM) Monitor (DataRAM, Mie Inc.)	Near-continuous mass concentrations of PM ₁₀ and PM _{2.5} .	1-hr	Daily	
Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corp.)	Size-fractionated PM ₁₀ mass, sulfate, nitrate	4-to-8 hr	6 th day	
MOUDI	Size-fractionated PM ₁₀ metals and elements	4-to-8 hr	6 th day	
MOUDI	Size-fractionated PM ₁₀ PAH, nitro-PAH	24-to-72 hr	6 th day	
MOUDI	Size-fractionated PM ₁₀ EC/OC	24-hour	6 th day	
High-Volume Particle Size Classifier (HVPSC)	Size-fractionated PM ₁₀ PAH, nitro-PAH	24-hour	6 th day	
PM ₁₀ and PM _{2.5} FRM (Andersen Samplers)	PM ₁₀ and PM _{2.5} mass, nitrate, sulfate concentrations	24-hour	6 th day	
PM ₁₀ and PM _{2.5} FRM	PM ₁₀ and PM _{2.5} EC and OC concentrations	24-hour	6 th day	
PM ₁₀ and PM _{2.5} Honeycomb Denuders Samplers (HDS)	PM ₁₀ and PM _{2.5} nitrate concentration	24-hour	6 th day	
PM ₁₀ and PM _{2.5} Multi-channel Denuder Sampler (MDS, Eatough et al, 1993)	PM ₁₀ and PM _{2.5} artifact-free EC/OC concentrations	24-hour	6 th day	
PM ₁₀ Time-of-Flight Mass Spectrometer	PM ₁₀ individual particle chemical composition	15 min, 1, 4, 12 and 24 hr	Daily on episodes, Riverside only	
Hering Low-Pressure Impactor (LPI, Hering and Friedlander, 1978)	Size distribution of particle-bound reactive oxidants and PM surface analysis	15 min, 1, 4, 12 and 24 hr	Selected sampling days	
Gaseous Pollutant Monitors				
Continuous Chemiluminescence Analyzer (Monitor Labs Model	Nitrogen Dioxide	15 min, 1, 4, 12 and 24 hr	Daily	

8840)			
Thermo Environmental Inc. Model 48C trace level	Carbon Monoxide	15 min, 1, 4, 12 and 24 hr	Daily
UV photometer (Dasibi Model 1003 AH)	Ozone	15 min, 1, 4, 12 and 24 hr	Daily
Continuous Ammonia Monitor (Thermo Env Inc. model 17C)	Ammonia	15 min, 1, 4, 12 and 24 hr	Daily
NMHC Thermo Environmental Inc., Model 55	Non-methane Hydrocarbons	hourly	Daily
Meteorology			
Vaisala Model MP113Y	Temperature and Relative Humidity	15 min, 1, 4, 12 and 24 hr	Daily
Met One High-Sensitivity Wind vane	Wind direction	15 min, 1, 4, 12 and 24 hr	Daily
Met One High Sensitivity Anemometer	Wind velocity	15 min, 1, 4, 12 and 24 hr	Daily

6

Proposed Timetable

Activity/Task	Year 1	Year 2	Year 3	Year 4	Year 5
Program Plan		_			
PIU installation at UCLA					
Development of new technologies instruments (HVPSC, CNSCM)					
PIU installation and operation in Mira Loma/Rubidoux					
PIU installation and operation at Downey					
PIU installation and operation in San Dimas/Azusa					
PIU installation and operation in Long Beach/Anaheim					
Chemical analysis					
Data validation and interpretation					

ABSTRACT

Particulate Matter "Supersites" Program - U.S. Environmental Protection Agency A joint solicitation of EPA's Office of Air and Radiation and Office of Research & Development Sorting Code: 99-NCERQA-X1

PM2.5 Technology Assessment and Characterization Study in New York (PMTACS-NY)

Principal Invesigator: Kenneth L. Demerjian ASRC, University at Albany
G. Lala, J. Schwab, V. Mohnen, and U. Roychowdhury, ASRC, University at Albany
P. Galvin, R. Gibbs, D. Felton and T. Lanni, New York State DEC
C. Kolb, M. Zanhiser, Aerodyne Research, Inc.
S. Herring, Aerosol Dynamics, Inc.
L. Newman, Brookhaven National Laboratories
P, Hopke, Clarkson University
W. Brune, Penn State University
L. Husain, N. Kim, X. Zhou, NYS Department of Health

J. Zamurs, NYS Department of Transportation
H. Patashnick, Rupprecht and Patashnick Co., Inc.

Project Period: Feburary 1, 2000 – December 1, 2004

Project Cost: Total Project Cost \$7,512,689; Total Request to EPA \$ 3,499,826.

Project Summary: The PMTACS-NY is designed to address a series of science policy relevant questions related to hypotheses to be tested using measurement data collected under the program.

Objective I. Measure the temporal and spatial distribution of the PM2.5/co-Pollutant complex including: SO₂, CO, VOCs/Air Toxics, NO, NO₂, O₃, NO_y, H₂CO, HNO₃, NH₃, HONO, PM2.5 (mass, SO₄⁼, NO₃⁻, OC, EC, Trace Elements), single particle aerosol composition, CN, OH and HO₂ to support regulatory requirements to develop cost effective mitigation strategies PM2.5 and its co-pollutants and to establish trends in the relevant precursor concentrations to assess the impact of recent and future emission reductions in terms of emission control effectiveness and air quality response.

Objective II. Monitor the effectiveness of new emission control technologies [i.e. Compressed Natural Gas (CNG) bus deployment and Continuously Regenerating Technology (CRT)] introduced in New York City and its impact on ambient air quality, thorough remote open path roadside, mobile platform, and fixed site measurements of CQ, CO, NO, H₂CO, HONO, CN and aerosol chemical composition.

Objective III. Test and evaluate new measurement technologies and provide tech-transfer of demonstrated operationally robust technologies for network operation in support of the development of process science and observation based analysis tools and health based exposure assessments.

Approach: Comprehensive measurement of PM2.5 mass, chemical speciation and gaseous precursors will be collected at six monitoring sites located in the New York City and at regional representative locations in upstate NY and operate through out the entire 5 year monitoring program. These sites include two regional research monitoring sites, Whiteface Mountain (Wilmington, NY) operational since 1973 and Pinnacle State Park (Addison, NY) operational since 1995 and three urban monitoring sites (NYS DEC SLAMS/PAMS sites), Mable Dean Bacon (Manhattan, NY), Intermediate School I.S. 155 (South Bronx, NY) and Queensborough Community College (Queens, NY). Standard routine measurements of criteria pollutants and the mandated PM2.5 mass and chemical speciationmeasurements, will be supplemented with advance instrumentation providing complimentary chemical and temporal specificity. The highly relevant measurements provided over the course of the program, fill a substantial data need associated with the characterization of the chemical composition of PM2.5 within New York City and the transport-impacted regional background of upstate NY.

Special intensive studies: In addition to the PMTACS, PM2.5 Supersite measurement network, two special intensive field studies will be carried out, the first in the summer of 2001 and the second in the winter of 2003. Both studies will be deployed from a host site that will likely be one of the urban measurement sites. The 4-6 weeks intensive studies will engage several research groups performing research grade measurements using emerging measurement technologies. The measurements will provide detailed real-time chemical and physical characterization of the PM/co-pollutant complex to 1) help elucidate the operative gas-to-particle transformation processes occurring in urban centers; 2) enhance the chemical source signature data base in support of source attribution studies; and 3) intercompare emerging technologies and evaluate their performance and in comparison with the operational routine measurement systems.

The CEPEX (CNG/CRT Emission Perturbation Experiments) performed as part of the special intensives, is designed to monitor on-road vehicle emissions of the CNG/CRT modified buses and traditional diesel-fueled buses being replaced, using open-path roadside remote sensing and a mobile measurement platform. In addition, the fixed-sitesupersite monitors will be used to discern changes in ambient air quality as a result of the implemented control technologies.

New PM2.5 instrumentation data will be used to evaluate/compare EPA FRM filter-based measurements and explore sources of error in the various approaches. The detailed data set of chemical and physical measurements of the PM2.5/co-pollutant complex in urban and regional environments will provide direct insights into the formation mechanisms for the PM2.5/co-pollutant complex and the controlling factors (chemical precursor, meteorological, and source attribution factors) that influence its production in the atmosphere. The suite of gaseous and chemical particulate measurements can be used to track, through direct observation, changes in precursor concentrations in response to implemented control programs, thereby supporting the concept of "Accountability in Air Quality Management Systems". These data will also be used by the health and regulatory communities in support of exposure assessments and the development of mitigation strategies.

Supplemental Keywords: ambient air, atmosphere, ozone, particulates, metals, nitrogen oxides, sulfates, organics, atmospheric chemistry, monitoring, measurement methods, Northeast.

PMTACS-NY "PROJECT AT A GLANCE"

PROJECT SITES	Major Activities by Year							
New York City:	2000	2001	2002	2003	2004			
Mabel Dean Bacon	Deploy and operate EPA designated criteria measurements ¹							
Special Studies: ^a	> Deploy and operate PM enhanced measurements ²							
		-OH/HO ₂ ³ -AMS/SPLAT APS ⁵ HONO/HNO ₃	⁴ -> ->	-OH/HO ₂ ³ -> -AMS/SPLAT ⁴ -> APS ⁵ > HONO/HNO ₃ ⁶ >				
	> Low T/Dryer TE(->	R&P 8400NS Field Testing & Evaluation ⁷						
Queensborough CC	> Deplo > R&P 840	y and operate PM enhar	riteria measurements ¹ nced measurements ² valuation ⁷					
	>							

2000 2001 2002 2003 2004					
2004					
Deploy and operate research grade baseline measurements ³					
Deploy and operate PM enhanced measurements ⁴					
>					
R&P 8400NS Field Testing & Evaluation ⁷					
>					
Low T/Dryer TEOM Field Testing & Evaluation ⁸					
D &D DDET Field Testing & Evaluation					
R&P DDET Field Testing & Evaluation ⁹					

PMTACS-NY "Project at a Glance" (continued)

PROJECT	Major Activities by Year							
SITES								
Upstate/	2000	2001	2002	2003	2004			
Regional:								
Whiteface	Deploy and operate research grade baseline measurements ²							
Mountain	>	>						
		Deploy and operate PM enhanced measurements ⁴						
		>						
Special	$-OH/HO_2^3 >$							
Studies:	R&P 8400NS Field Testing & Evaluation ⁷							
	>							
	Low T/Dryer TEOM Field Testing & Evaluation ⁸							
	>							
	R&P DDET Field Testing & Evaluation ⁹							
	>							

^a Special intensive studies will be performed at one of the three urban sites identified in NYC, final selection will be made early in 2000 in consultation with NYSDEC, EPA and special study collaborators.

¹ Measurements to be performed and specifications are summarized in Table 1.

² Enhanced measurements to be performed and specification are summarized in Table 1 and details of the new technologies are described in Table 2.

³ PSU GTHOS OH/HO₂ intensive study measurement, details of the new technology are described in Table 2.

⁴ Single particle aerosol chemical composition as a function of size, intensive study measurement, details of the new technologies are described in Table 2

⁵ Aerosol size distribution intensive study measurements

⁶ NYSDOH HONO/HNO₃ Analyzer intensive study measurement, details of the new technology are described in Table 2.

⁷ PM2.5 nitrate and sulfate analyzer under commercial development by R&P, details of the new technology are described in Table 2, deployment beyond 2001 assumes acceptable performance based on 2000-2001 field testing and evaluation.

⁸ PM2.5 T&RH modified R&P TEOM, details of the new technology are described in Table 2, deployment beyond 2001 assumes acceptable performance based on 2000-2001 field-testing and evaluation.

⁹ PM2.5 Differential Dual EPS TEOM, under commercial development by R&P, details of the new technology are described in Table 2, deployment beyond 2001 assumes acceptable performance based on 2000-2001 field testing and evaluation.

¹⁰ Photochemical Assessment Monitoring Station, measurements to be performed and specifications are summarized in Table 1.

¹¹ Aerodyne Research, Inc mobile laboratory intensive study measurements, details of the new technology are described in Table 2.

¹² TILDAS open path crossroad remote measurements; details of the new technology are described in Table 2.

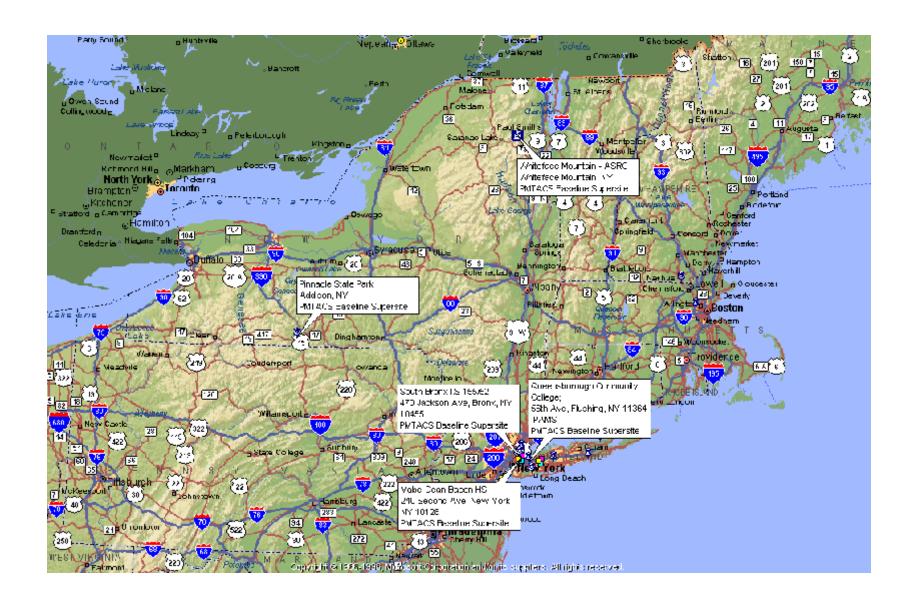


Figure 3. PMTACS-NY Supersite Network



Figure 4. PMTACS-NY Urban Supersites

TABLE 1. PMTACS-NY Sites, Measurement Parameters And Specifications

Parameter/Method	Sites*	Operator**	Period	Averaging	Frequency
PM Filter Mass and Chemistry					
PM2.5 mass, sulfate, nitrate /Ion	WFML	DEC, ASRC	April 1, 2000 -	24-hr	daily
Chromatograph PM2.5 (Chemical Species Measurements, as	QCC	DEC Analytical	December 1, 2004 April 1, 2000 –	24-hr	3 rd day
outlined in EPA, 1999)	QCC	Lab (to be decided)	December 1, 2004	24-111	3 day
PM10 mass, sulfate, nitrate /Ion Chrom	WFML, MDB, SB	DEC, ASRC	April 1, 2000 – December 1, 2004	24-hr	6 th day
PM2.5 mass (FRM-R&P Partisol Sampler)	PSP, WFML, MDB, SB, QCC	DEC, ASRC	April 1, 2000 – December 1, 2004	24-hr	daily
PM2.5 metals Mg, Al, K, Ca, V, Cr, Mn, Ni, Fe, Zn, As, Se, Cd, Sb, Hg, and Pb /ICP/AES, ICP/MS, & neutron activation	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, DOH	July 1, 2000 – June 30, 2001	24-hr	daily
PM2.5 SO ₄ ⁼ , NO ₃ ⁻ , NO ₂ ⁻ , Cl, Br /Ion Chromatograph	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, DOH	July 1, 2000 – June 30, 2001	24-hr	daily
PM2.5 metals Mg, Al, K, Ca, V, Cr, Mn, Ni, Fe, Zn, As, Se, Cd, Sb, Hg, and Pb/ XRF	PSP, MDB, SB, QCC, NNJ	DEC, ASRC	July 1, 2001 – December 1, 2003	24-hr	6 th day
PM2.5 SO ₄ ⁼ , NO ₃ ⁻ , NO ₂ ⁻ , Cl, Br /Ion Chromatograph	PSP, MDB, SB, QCC, NNJ	DEC, ASRC	July 1, 2001 – December 1, 2003	24-hr	6 th day
PM2.5 metals Mg, Al, K, Ca, V, Cr, Mn, Ni, Fe, Zn, As, Se, Cd, Sb, Hg, and Pb /ICP/AES, ICP/MS, & neutron activation	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, NYSDOH	Intensive: 4 weeks ea. Summer 2001 Winter 2003	6-hr	daily
PM2.5 SO ₄ ⁼ , NO ₃ ⁻ , NO ₂ ⁻ , Cl, Br /Ion Chromatograph	PSP, MDB, SB, QCC, NNJ	DEC, ASRC, DOH	Intensive: 4 weeks ea. Summer 2001 Winter 2003	6-hr	daily
PM10/PM2.5 Particle Concentrator (R&P ChemTox Model 2400)	PSP MDB or SB	DEC, ASRC	Seasonal year 2000 Seasonal 2001-2003	variable	variable

Table 1. PMTACS-NY Sites, Measurement Parameters and Specifications (continued)

Continuous PM Mass and Chemistry	arameters and Spec	lications (contin	ueu)		
PM2.5 mass (heated R&P TEOM 1400AB)	PSP, WFML, MDB, SB, QCC	DEC,ASRC	June 1, 2000 – December 1, 2004	10-min	daily
PM10 mass (heated R&P TEOM 1400AB)	MDB, SB	DEC,ASRC	ĺ	10-min	daily
PM2.5 mass (T/RH modified R&P TEOM 1400AB)	PSP, WFML, MDB	DEC,ASRC	June 1, 2000 – May 31, 2003	10-min	daily
PM2.5 mass (Differential ESP R&P TEOM)	PSP, MDB	ASRC	June 1, 2001 – December 31, 2004	5-min	daily
PM2.5 nitrate and sulfate (R&P flash volatilization 8400NS)	PSP, WFML, MDB, SB, QCC	DEC,ASRC	(3) June 1, 2000 - (2) June 1, 2001 – December 1, 2004	10-min	daily
PM2.5 Organic and elemental carbon (R&P 5400)	PSP, WFML, MDB, SB, QCC	DEC,ASRC	June 1, 2001 – December 1, 2004	1-hr	daily
Single particle chemical speciation (Aerodyne, Inc Aerosol Mass Spectrometer [AMS])	MDB/QCC	ASRC	Intensive: 4 weeks ea. Summer 2001 Winter 2003	TBD	TBD
Single particle chemical speciation (BNL Single Particle Laser Ablation Time of Flight Mass Spectrometer [SPLAT-MS])	MDB/QCC	BNL	Intensive: 4 weeks ea. Summer 2001 Winter 2003	TBD	TBD
NO - TECO 42s	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	April 1, 2000 – December 1, 2004	5-min	daily
NO2-photolytic titration modified TECO 42s	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	June 1, 2000 – December 1, 2004	5-min	daily
NOy Moly. Modified TECO 42s	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	June 1, 2000 – December 1, 2004	5-min	daily
SO2 TECO 43b	PSP, WFMS, MDB, SB, QCC	DEC,ASRC	April 1, 2000 – December 1, 2004	5-min	daily
O3 TECO	PSP, WFML, MDB, SB, QCC	DEC,ASRC	April 1, 2000 – December 1, 2004	5-min	daily

Table 1. PMTACS-NY Sites, Measurement Parameters and Specifications (continued)

CO Modified TECO 48s	PSP, WFMS,	DEC,ASRC	June 1, 2000 – December 1, 2004	5-min	daily
NO/CO or H2CO/HONO open path TILDAS	MDB, SB, QCC MDB/QCC	DEC,ASRC, Aerodyne	Intensive: 4 weeks ea. Summer 2001 Winter 2003	5-min	daily
OH/HO2 LIF	WFM MDB/QCC	PSU	Intensives: 4 weeks ea. Summer 2000 – WFM Summer 2001 - MDB Winter 2003 - MDB	10-min	daily
HONO/HNO3 scrubbed derivatization HPLC	MDB/QCC	DOH	Intensive: 4 weeks ea. Summer 2001 Winter 2003	5-min	daily
Hydrocarbons C2-C10 Canisters GC/FID	WFMS, WFML	ASRC	May 15, 2000 – December 1, 2004	3-hr integrated	2 nd day in Summer; weekly in winter
Hydrocarbons C2-C10 PE Auto GC	PSP, QCC	ASRC, DEC	May 15 - October 15 2000-2004	40-min	daily summer
H2CO /AEROLaser 14001A and/or TexasTech	PSP, WFML, MDB, SB, QCC	DEC, ASRC	12 week Summer Intensives: 2000-04 6 week Winter Intensives: 2000-2003	5-min	daily
Air Toxics	MDB/QCC; SB	DEC	Seasonal 2000-04	24-hr	3 rd day

Table 1. PMTACS-NY Sites, Measurement Parameters and Specifications (continued)

Particle Number, Size & Optical Properties					
Condensation Nuclei Counter/ TSI 3025A	MDB, SB, QCC	DEC	April 1, 2000 –	5-min	daily
(0.003μm to 1 μm)			December 1, 2004		
Condensation Nuclei Counter/ GE	PSP, WFML	ASRC	April 1, 2000 –	5-min	daily
			December 1, 2004		
Aerosol Size Distribution (0.003μm to 1 μm) /			4 week Summer		
TSI 3934	PSP. MDB/SB	ASRC	Intensives: 2000-2003	5-min	daily
			4 week Winter		
			Intensives: 2000-2003		
Aerodynamic Particle Sizer Spectrometer			4 week Summer		
(0.37μm to 20 μm) / TSI 3320	PSP, MDB/SB	ASRC, DEC	Intensives: 2000-2003	5-min	daily
			4 week Winter		
			Intensives: 2000-2003		
Aerosol Light Absorption/ Aethalometer	PSP, MDB/SB	ASRC, DEC	January 1, 2001 –	5-min	daily
(elemental carbon)			December 31, 2003		
Aerosol Light Scattering: 3-color integrating	PSP, MDB/QCC	ASRC, DEC	January 1, 2001 –	5-min	daily
nephelometer /TSI 3563 or equivalent system			December 31, 2003		
Meteorological Measurements					
Wind speed and direction, temperature,	PSP, WFMS,	DEC,ASRC	April 1, 2000 –	5-min	daily
barometric pressure, relative humidity	MDB, SB, QCC		December 31, 2004		

*Sites -

Whiteface Mountain Summit and Lodge: WFMS, WFML

Pinnacle State Park: PSP Mable Dean Bacon: MDB

I.S. 155 South Bronx: SB Queensborough Community College: QCC

Northern NJ site to be designated

** Operators –

Aerodyne Research, Inc: ARI

Atmospheric Sciences Research Center: ASRC

Brookhaven National Laboratories: BNL

NYS Department of Environmental Conservation: DEC

NYS Department of Health: DOH Pennsylvania State University: PSU

ABSTRACT

Title: The Pittsburgh PM Supersite Program: A Multi-Disciplinary Consortium for Atmospheric Aerosol Research

Investigators: Spyros Pandis, Cliff Davidson, Allen Robinson (*Carnegie Mellon Univ.*), Anthony Wexler, Murray Johnston (*Univ. of Delaware*), Wolfgang Rogge (*Florida Intern. Univ.*), Mark Hernandez (*Univ. of Colorado*), Jeff Collett (*Colorado State Univ.*), Susanne Hering (*Aerosol Dynamics*), Jonathan Kahl (*Univ. Wisconsin*), Barbara Turpin (*Rutgers Univ.*), John Ondov, Steven Buckley(*Univ. of Maryland*), *RJ Lee, Inc.*, Kevin Crist (*Ohio University*), Antonio Miguel (*Univ. Calif. Riverside*), Delbert Eatough (*Brigham Young University*), Urs Baltensperger (*Paul Scherrer Inst.*), Jonathan Samet (*Johns Hopkins*), Richard Sextro (*Lawrence Berkeley Nat. Lab*), Thomas Feeley (*DOE-NETL*).

Institutions: Carnegie Mellon University, Pittsburgh, Pennsylvania – University of Delaware, Newark, Delaware - Florida International University, Miami, Florida - University of Colorado, Boulder, Colorado – Colorado State University, Ft. Collins, Colorado – Aerosol Dynamics, Berkeley, California – University of Wisconsin, Milwaukee, Wisconsin – Rutgers University, New Brunswick, New Jersey – University of Maryland, College Park, Maryland - RJ Lee, Monroeville, Pennsylvania - Ohio University, Athens, Ohio - University of California, Riverside, California - Brigham Young University, Provo, Utah - Paul Scherrer Institute, Villigen, Switzerland – Johns Hopkins University, Baltimore, Maryland – Lawrence Berkeley Nat. Lab, Berkeley, California – DOE/NETL, Pittsburgh, Pennsylvania.

Project Period: January, 2000 – December, 2004

Project Cost: \$3,500,000

Project Summary: Airborne particulate matter (PM) continues to pose serious health risks for susceptible members of the U.S. population and for sensitive ecosystems. Design of cost-effective PM control strategies is limited by the lack of understanding of the PM-health effects links which is exacerbated by a paucity of physiological data, the difficulty of establishing the PM source-receptor relationships, and finally the limitations of existing instrumentation for PM measurements. A comprehensive multidisciplinary study is proposed for the Pittsburgh region, which will address all of the above issues.

The proposed hypothesis-driven program will have six components:

- Ambient monitoring in a central supersite and a set of satellite sites in the region (leveraged against Department of Energy Federal Energy Technology Center (DOE/FETC) funds).
- An epidemiological study (to be leveraged against funds from NIH and others).
- An indoor monitoring study (extension of work currently funded by DOE and EPA).
- An instrument development and evaluation study (leveraged against current NSF and other EPA funds).
- A comprehensive modeling component (currently funded by the EPA STAR program).
- A data analysis and synthesis component (hypothesis testing).

In addition to the above resources the program leverages funds and resources from local industry (Bayer), local government (Allegheny County Health Department), state government (Pennsylvania Department of Environmental Protection), and cost sharing by Carnegie Mellon University.

The objectives of the EPA-funded part of the Pittsburgh Supersite Program are: to characterize PM (size, surface, and volume distribution, chemical composition as a function of size and on a single particle

basis, morphology, and temporal and spatial variability) in the Pittsburgh region; to quantify the impact of the various sources (transportation, power plants, biogenic, etc.) to the PM concentrations in the area; and to develop and evaluate the next generation of atmospheric aerosol monitoring techniques (single particle measurements, continuous composition measurements, ultrafine aerosol measurements, improved organic component characterization, etc.). Combining the ambient monitoring study supported by the EPA Supersites program with the proposed indoor, health, and modeling studies (funded by other sources) will allow the proposed program to: elucidate the links between PM characteristics and their health impacts; quantify the relationship between indoor and outdoor concentrations; and quantify the responses of PM characteristics to changes in emissions to support SIP development. These objectives address all the goals of the EPA Supersites Program and will be achieved through the investigation of approximately twenty hypotheses addressing issues in ambient aerosol characterization, measurement methods, atmospheric processes, aerosol properties, source-receptor relationships, health effects, and indoor exposure.

The measurement program will feature a central supersite located in Pittsburgh near the CMU campus and a set of satellite sites. Baseline monitoring is planned for an 18-month period that will include detailed characterization of PM size, surface, and volume distributions, chemical composition as a function of size, continuous single-particle size and composition measurements, organic aerosol speciation, measurement of the distribution and composition of ultrafine aerosols, semi-continuous measurements of metals, nitrate, sulfate, and aerosol carbon, measurements of bioaerosols, aerosol precursors, cloud and fog composition in the area, aerosol optical and hygroscopic properties, and meteorological variables. Three intensive sampling periods are planned to examine temporal variations and to collect detailed data for model testing and validation. The data from this project will be made available through an easily accessible electronic database. The Supersite team with the help of the CMU Computer Science School will post "immediately" the available raw data (real-time and continuous measurements) and the remaining data as soon as they become available to a web site accessible by the EPA researchers. This rapid exchange of information will facilitate the collaboration with our EPA colleagues. Throughout the program, we will look for opportunities to minimize adverse environmental effects of the sampling effort without compromising the quality of the data.

The following benefits are expected from the Pittsburgh Supersite program:

- Comprehensive characterization of the PM in the Pittsburgh area. This will include, size distribution, composition as a function of size and for individual particles, temporal and spatial variation, optical and hygroscopic properties, and morphology.
- Development and evaluation of state-of-the-art instrumentation and measurement approaches (single particle instruments, continuous measurement approaches, etc.)
- Apportionment of the measured PM (both primary and secondary) to sources as a function of time. These results should be valuable for SIP development.
- Establishment of links between the PM characteristics and health effects in the study area.
- Quantification of the relationship between indoor and outdoor PM levels in the region.
- Development of a dataset (in coordination with the other Supersites) for the evaluation of the approaches used for the description of PM processes in atmospheric chemistry models.

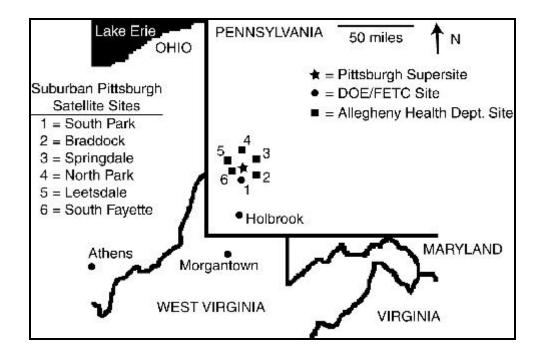


Figure 1. Map of Pittsburgh region showing the approximate location of the Supersite, the four DOE/NETL UORVP sites that will be used as satellite sites, and five candidate satellite sites that are currently Allegheny County Health Department sampling sites.

		20	000			20	01			20	02			20	03	
Task	W	Sp	Su	F	W	Sp	Su	F	W	Sp	Su	F	W	Sp	Su	F
Site							•	•	•		•	•	•			-
Site preparation																
Site restoration																
QA/QC																
Finalize QA/QC																
Qual. Management Plan																
Sampling																
Baseline																
Intensives																
Data Analysis																
Preliminary analysis																
Hypothesis testing																
Reporting																
Planning reports																
Progress reports																
Final report																
Additional Studies																
Indoor Study																
Epidemiology																

 Table 1. Measurements in the Pittsburgh Supersite Program

Measurements	Instrumentation	Frequency Regular	Frequency Intensives	Investigator
Aerosol number distribution	Ultrafine SMPS ¹ , SMPS ² , APS ³ , ELPI ⁴ , Ultrafine CPC ⁵	10 min	5 min	Pandis
Aerosol surface distribution	Ultrafine SMPS, SMPS, APS, ELPI, Ultrafine CPC, Epiphaniometer	10 min	5 min	Pandis
Aerosol volume Distribution	Ultrafine SMPS ,SMPS, APS, ELPI, Ultrafine CPC	10 min	5 min	Pandis
PM _{2.5} mass	FRM ⁶ , TEOM ⁷ , CMU Sampler ⁸ , LPI ⁹ , MOUDI ¹⁰	1 day	4-6 hr	Davidson
PM ₁₀ mass	FRM, TEOM, CMU Sampler, LPI, MOUDI	1 day	4-6 hr	Davidson
PM _x mass	LPI, MOUDI	1 day	4-6 hr	Davidson
PM _{2.5} ions and elements	CMU Sampler/ IC 11 & ICPMS12	1 day	4-6 hr	Davidson
PM _{2.5} -10 ions, elements	CMU Sampler/ IC & ICPMS	1 day	4-6 hr	Davidson
HNO ₃ vapor	CMU Sampler/ IC & ICPMS	1 day	4-6 hr	Davidson
NH ₃ vapor	CMU Sampler/ IC & ICPMS	1 day	4-6 hr	Davidson
Size-resolved ions and	MOUDI/IC and ICPMS	-	4-6 hr	Davidson
metals				
PM _{2.5} OC and EC ¹³	Organic sampler/thermal	1 day	4-6 hr	Robinson
	PC-BOSS system ¹⁴	-	4-6 hr	Eatough
	In-situ carbon analyzer	-	1-2 hr	Turpin
PM ₁₀ OC and EC	Organic sampler/thermal	1 day	4-6 hr	Robinson
	R&P sampler ¹⁵	1 hr	1 hr	Robinson
PM _x OC and EC	ELPI/thermal	-	4-6 hr	Robinson
Organic speciation	Organic sampler/GC-MS ¹⁶	2 weeks	4-12 hr	Rogge
Organic size-resolved characterization	LPI/FTIR ¹⁷	-	24 hr	Turpin
Polycyclic Aromatic Hydrocarbons	MOUDI-PUF system ¹⁸ /GC-MS, HPLC ¹⁹ -fluorescence	-	12 hr	Miguel
Polar Organics	RSMS-II ²⁰	Continuous	Continuous	Wexler
Single Particle	RSMS-II	Continuous	Continuous	Wexler
Chemical Composition	Filter/SEM ²¹	-	4-6 hr	RJ Lee
	LIBS	-	Continuous	Buckley
Semi-continuous metals	HFAS/GFAA ²²	-	10-60 minutes	Ondov
Continuous nitrate	ICVC	Continuous	Continuous	Hering
Continuous sulfate	ICVC	Continuous	Continuous	Hering
Continuous carbon	ICVC	Continuous	Continuous	Hering
Bioaerosols	Epi-fluorescent microscopy,	1 day	Variable	Hernandez

	Molecular biology assays			
Visibility	Nephelometer	Continuous	Continuous	Pandis
	Photos/Visual Range	6 hr	1 hr	
Growth with RH	TDMA ²³ /RSMS-II	Variable	Variable	Pandis
CCN concentration	CCN Counter 24	Variable	Variable	Pandis
RH, T, Wind		Continuous	Continuous	Davidson
UV and Solar		Continuous	Continuous	Pandis
Trajectories		1 day	4 hr	Kahl
VOCs	GC-FID ²⁵ , GC-MS	6 days	4-6 hr	Pandis
Hydrogen Peroxide	CSU Monitor	12 hr	1 hr	Collett
Organic Peroxides	CSU Monitor	12 hr	1hr	Collett
O_3	Ozone Monitor	1 hr	1 hr	Pandis
NO and NO ₂	NOx Monitor	1 hr	1 hr	Pandis
SO_2	SO ₂ Monitor, Filter	1 hr	1 hr	Pandis
CO	CO Monitor	1 hr	1 hr	Pandis
Fog and cloud	CSU Collector ²⁶	Variable	1 hr	Collett
composition				

¹ Ultrafine SMPS: Scanning Mobility Particle Spectrometer (TSI model 3936N25) for 0.003-0.150 μm

 $^{^2}$ SMPS: Scanning Mobility Particle Spectrometer (TSI model 3934L) for 0.01-1.0 μm

 $^{^3}$ APS: Aerodynamic Particle Sizer Spectrometer (TSI model 3320) for 0.5-1.0 μm

⁴ ELPI: Electrical Low Pressure Impactor (Dekati)

 $^{^5}$ Ultrafine CPC: Ultrafine Condensation Particle Counter (TSI model 3025A) for 0.003-10 μm

⁶ FRM: Federal Reference Method PM_{2.5} Sampler

⁷ TEOM: Tapered Element Oscillating Microbalance PM_{2.5} Sampler

⁸ CMU Sampler: Carnegie Mellon University system shown in Figure 2

⁹ LPI: Low Pressure Impactor developed by Susanne Hering

¹⁰ MOUDI: Micro-Orifice Uniform Deposit Impactor

¹¹ IC: Ion Chromatography

¹² ICPMS: Inductively Coupled Plasma Mass Spectrometer

¹³ OC and EC: Organic Carbon and Elemental Carbon

¹⁴ PC-BOSS: Particle Concentrator-Brigham Young University Organic Sampling System.

¹⁵ R&P sampler: Ruprecht and Patashnik sampling system

¹⁶ GC-MS: Gas Chromatography-Mass Spectrometry

¹⁷ FTIR: Fourier Transform Infrared Spectroscopy

¹⁸ MOUDI-PUF system: MOUDI-Polyurethane Foam plug preceded by a cyclone and denuder

¹⁹ HPLC: High Performance Liquid Chromatography

²⁰ RSMS-II: University of Delaware Single Particle Mass Spectrometer

²¹ SEM: Scanning Electron Microscopy

²² HFAS/GFAA: High Frequency Aerosol Sampler/Graphite Furnace Atomic Absorption Spectrophotometry

²³ TDMA: Tandem Differential Mobility Analyzer

²⁴ CCN Counter: Cloud Condensation Nuclei Counter manufactured by DH Associates

²⁵ GC-FID: Gas Chromatography-Flame Ionization Detector

²⁶ CSU collector: Colorado State University cloudwater collector

ABSTRACT

<u>Title:</u> St. Louis-Midwest Supersite

Investigators and Institutions

Dr. Jay Turner, PI Washington University, St. Louis, MO Dr. Judith Chow, Co-PI Desert Research Institute, Reno, NV Dr. Petros Koutrakis, Co-PI Harvard University, Cambridge, MA Dr. Peter McMurry, Co-PI University of Minnesota, Minneapolis, MN Dr. John Ondov, Co-PI University of Maryland, College Park, MD Dr. James Schauer, Co-PI University of Wisconsin, Madison, WI Dr. Warren White, Co-PI Washington University, St. Louis, MO Mr. George Allen Harvard University, Cambridge, MA

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Project Period: January 1, 2000 through December 31, 2003

<u>Project Cost:</u> \$ 3,883,566

Project Summary

A fine particulate matter Supersite is proposed in Metropolitan St. Louis (IL-MO), a major industrial and population center. This comprehensive research program will provide physical and chemical measurements needed by the health effects, atmospheric science and regulatory communities, in a setting broadly representative of the urban Midwest. The proposal is submitted by a public/private partnership that provides significant leveraging of resources.

Measurements will be fully integrated with three large health effects programs: the EPA/Harvard Center on Ambient Particle Health Effects, the NIEHS/Harvard Program Project on Ambient Particles Cardiac Vulnerability, and the EPRI Particle Exposure Assessment Program. These health studies will: (i) investigate relationships between personal exposures and outdoor concentrations, and examine the health effects of chronic exposures; (ii) identify biological mechanisms responsible for particle health effects; (iii) identify susceptible populations; and (iv) investigate the relative toxicity of the different particle constituents.

The measurement strategy features sustained sampling using state-of-the-art continuous monitoring techniques for particle mass, size and composition. The high time resolution of the data will permit novel hypotheses and interpretive techniques to be tested in both source apportionment and health effects studies. Measurements will be conducted throughout a full year at the core site, located in an urban residential neighborhood of St. Louis City, providing context for episodes and to support the time series epidemiological studies. A movable instrument platform will rotate between four satellite sites in the greater St. Louis region, collecting 21-24 successive days of measurements at each site during each season. The satellite sites will be used to examine the impacts of local sources and to investigate the spatial patterns of outdoor exposures. Emphasis in designing the measurement platforms has been placed on identifying

advanced methods with demonstrated or potential ability to operate reliably for extended periods with limited attendance.

In situ measurements will obtain temporally resolved data for particle size, mass, nitrate, sulfate, organic and elemental carbon, and five metals of environmental significance. Instrumentation newly developed at the University of Minnesota will continuously measure particle size distributions as well as integral moments of the particle size distribution (range $3~\text{nm}-10~\text{\mu m}$). The latter method shows promise as a cost-effective approach for obtaining particle size data for health effects studies, and will be validated using conventional particle sizing techniques. Continuous instruments developed by Harvard University for particle mass, nitrate and sulfate will be deployed at both the core and satellite sites to provide data for health effects studies and assessing temporal and spatial variability. A semi-continuous carbon analyzer will be used at the core site to obtain hourly average elemental and organic carbon concentrations. A novel semi-continuous elemental analysis system developed by the University of Maryland will be operated at the core site to provide hourly-average data for five heavy metals of significant interest to the health effects and source apportionment communities. The experience to be gained through the field testing of these advanced monitoring techniques will be shared with the scientific and instrument manufacturing communities.

Substrate methods will be used for 24-hour integrated measurements of particle mass and composition. These measurements will feature enhancements to the chemical speciation network methods and will be used to: (a) evaluate the continuous monitoring techniques; and (b) provide detailed chemical characterization of particles beyond the baseline analyses for the chemical speciation network (precursor gases, particle acidity, an expanded suite of particulate ions, and water soluble metals). Elemental analysis strategies are emphasized because of their importance to health effects and source apportionment studies. Collocated samples will be used to compare four distinct analytical methods - XRF, ICPMS, INAA and GFAA. Based on the results, one method will be chosen to analyze the full year of daily samples for both the core and satellite sites. 24-hour integrated measurements at both sites will provide data to: (a) evaluate the performance of the continuous monitors in various environments; (b) investigate temporal and spatial variations in particle mass and composition; and (c) support the health effects studies.

Samples will also be collected for retrospective analysis of trace element and organic compound composition. About 500 one-hour integrated samples will be analyzed for twelve trace elements in addition to the sustained hourly-average measurements for five elements. Detailed organic speciation will be performed for more than 100 of the 24-hour integrated samples. These analyses will provide data to support both health effects and source apportionment studies.

A consortium of six universities from across the country has been assembled to undertake the proposed St. Louis Supersite program. The investigators include experts in methods development, particle chemistry and physics, field studies, data processing and analysis, source apportionment, exposure assessment, and quality assurance. The Principal Investigator – Dr. Jay Turner of Washington University – will work closely with the Executive Management Team consisting of Dr. Judith Chow (Desert Research Institute), Dr. Petros Koutrakis (Harvard University), Dr. Peter McMurry (University of Minnesota) and Dr. Warren White (Washington University) to guarantee successful execution of this project.

This proposed project runs from January 2000 through December 2003. First year activities focus on study planning and design with measurements phased in during the 4th Quarter. Sustained monitoring with the full suite of measurements will be conducted from January 1, 2001, through December 31, 2001. The two remaining years will be used for chemical characterization, data analysis and reporting.

Proposed measurements for the St. Louis - Midwest Supersite - aerosol physical properties. 1

	Size Range	Duration	Core	Satellite
Aerosol Size Distribution				
Nano-Scanning Mobility Particle Spectrometer (SMPS) (University of Minnesota)	3-20 nm	5 min	X	
Scanning Mobility Particle Spectrometer (SMPS) (University of Minnesota)	20-500 nm	5 min	X	
LasAir Optical Particle Counter (University of Minnesota)	0.2-2 μm	5 min	X	
Aerodynamic Particle Sizer (University of Minnesota)	0.3-10 μm	5 min	X	
Integral Moments of Physical Aerosol Prop	erties			
Number Concentration (TSI 3025 Ultrafine CPC) (University of Minnesota)	>3 nm	2 sec	X	X
"Dry" Light Scattering Coefficient (Nephelometer) (University of Minnesota)	<2.5 μm	2 sec	X	X
Electrical Charge Integral (University of Minnesota)	<2.5 μm	2 sec	X	X
Transmittance through filter deposits (Aethalometer) (Harvard University)	<2.5 μm	5 min	X	X
Total Mass Concentration (CAMMS) (Harvard University)	<2.5 µm	1 hour	X	X

Substrate Methods (Time-Integrated Man	ually-Operated	Substrate Methods (Time-Integrated Manually-Operated Samplers)						
Particle Mass Concentration	Size Range	Duration	Core	Satellite				
Harvard Impactor (Harvard University)								
- PM ₁	<1.0 µm	24 h	X	X				
- PM _{2.5}	<2.5 µm	24 h	X	X				
- PM ₁₀	<10 µm	24 h	X	X				
HEADS (Harvard University)								
- PM _{2.5}	<2.5 µm	24 h	X	X				
Sequential FRM (City of St. Louis)								
- PM _{2.5}	<2.5 µm	24 h	X	$(X)^2$				
Non-Sequential FRM (City of St. Louis)								
- PM ₁₀	<10 µm	24 h	X	(X) ²				
		(1-in-6 days)						

High Resolution Dichotomous Sampler				
(Harvard University)				
- fine PM (PM _{2.5})	<2.5 μm	24 h	X	X
- coarse PM (PM ₁₀ – PM _{2.5})	2.5-10 μm	24 h	X	X

Proposed measurements for the St. Louis - Midwest Supersite - aerosol chemical properties.¹

In Situ Measurements (Semi-Continuous Automated Measurements)						
	Size Range	Duration	Core	Satellite		
Sulfate (e.g., R&P/ADI, HSPH, ARA)	<2.5 µm	10 min	X	X		
(Harvard University)						
Nitrate (e.g., R&P/ADI, HSPH, ARA)	< 2.5 µm	10 min	X	X		
(Harvard University)						
OC/EC (Sunset Laboratory Instrument)	<2.5 μm	1 hour	X			
(University of Wisconsin)						

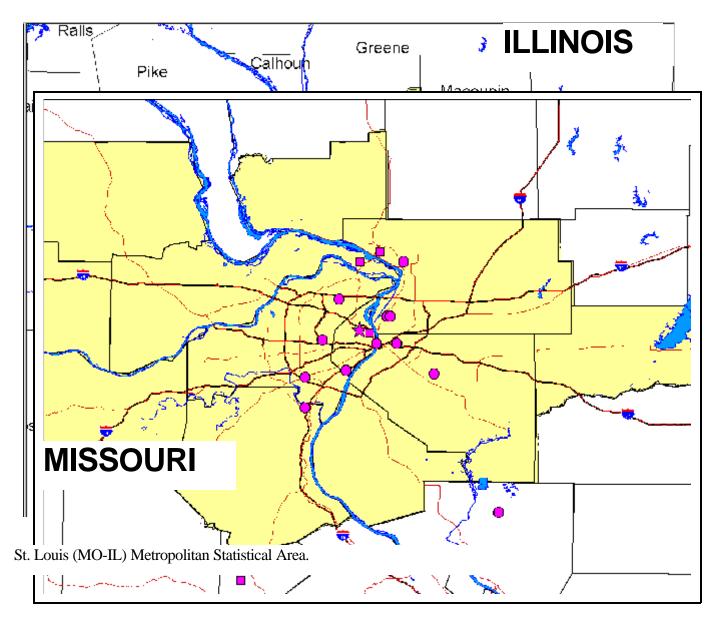
Substrate Methods (Time-Integrated Manu	ually-Operated	l Samplers)		
_	Size Range	Duration	Core	Satellite
HEADS: sulfate, nitrate, ammonium, potassium and sodium ions, acidity, ammonia, nitric/nitrous acid, SO ₂ (Harvard University)	<2.5 µm	24 hour	X	X
OC/EC (NIOSH method 5040) (University of Wisconsin)	<2.5 μm	24 hour	X	X
Trace Metals (analytical method to be determined)	<2.5 μm	24 hour	X	X
Coarse PM Trace Metals ³ (analytical method to be determined)	<10 μm - or - 2.5-10 μm	24 hour	X	X
12 ⁺ elements (from As, Cu, Mn, Ni, Cr, Cd, Se, Ag, Pb, Al, Fe, Zn, Ca, V, Ti, Be, Ba) (HFASS-GRAAZ) (University of Maryland)	<2.5 µm	1 hour (retrospective analysis @ ~1200 samples)	X	
Organic compound speciation (University of Wisconsin)	<2.5 µm	24 hour (retrospective analysis @ ~110 samples)	X	
Toxicological sampling (1630 m³ sampling volume) (Harvard University)	<2.5 µm	1 week (retrospective analysis)	X	

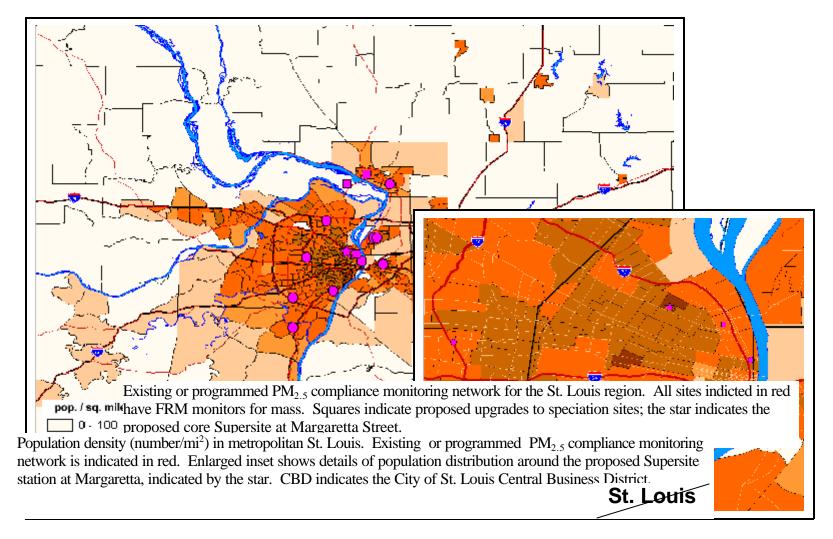
Proposed measurements for the St. Louis - Midwest Supersite - other measurements.¹

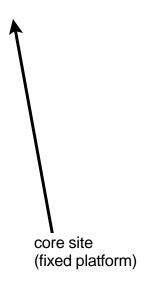
	Duration	Core	Satellite
Airborne Bioallergens	24 hour	Clayton, MO	
(St. Louis County and Washington University)			
Meteorological Parameters	5 min	X	
(Washington University)			
- wind speed			
- wind direction			
- temperature			
- relative humidity			
- barometric pressure			
- solar radiation			
Criteria Gas Pollutants	1 hour	X	$(\mathbf{X})^1$
(City of St. Louis)			
- nitric oxide / nitrogen oxides			
- ozone			
- carbon monoxide			
- sulfur dioxide			

FOOTNOTES:

- (1) All measurements will be sustained for an entire year. Thus, the sampling frequency is the reciprocal of the duration (e.g., 24 hour samples will be collected 1/day, hourly samples will be collected 24/day) unless other noted.
- (2) Criteria gaseous pollutants, PM_{2.5} and PM₁₀ will be available at satellite sites collocated with compliance network monitors. Responsible agencies include the City of St. Louis, St. Louis County, Missouri Department of Natural Resources, and Illinois Environmental Protection Agency.
- (3) Analysis of either PM₁₀ samples or dichotomous sampler coarse filter samples.







plus three satellite sites, each visited by a movable platform for 3-4 weeks per quarter (locations TBD)